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# A LABORATORY INVESTIGATION OF TRACE METAL ADSORPTION ON A MARINE SEDIMENT IN SEA WATER AND THE SPECIATION OF COPPER IN SEA WATER

DAVID ALLAN STERN

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A LABORATORY INVESTIGATION OF TRACE METAL ADSORPTION  
ON A MARINE SEDIMENT IN SEA WATER  
AND THE SPECIATION OF COPPER IN SEA WATER

by

DAVID ALLAN STERN

B. S., Lafayette College, 1968

A THESIS

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This thesis has been examined and approved.

Clarence L. Grant

Clarence L. Grant, Prof. of Chemistry  
Thesis Director

Albert F. Daggett

Albert F. Daggett, Prof. of Chemistry

Helmut M. Haendler

Helmut M. Haendler, Prof. of Chemistry

James H. Weber

James H. Weber, Assoc. Professor  
of Chemistry

Paul L. Bishop

Paul L. Bishop, Asst. Professor  
Civil Engineering

12/12/74

Date

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I dedicate this Thesis to

My Wife, Bonnie,

for all her love and patience.

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## ABSTRACT

### A LABORATORY INVESTIGATION OF TRACE METAL ADSORPTION ON A MARINE SEDIMENT IN SEA WATER AND THE SPECIATION OF COPPER IN SEA WATER

by

DAVID ALLAN STERN

Several trace metals such as copper, lead, and zinc are essential to marine life at normal concentrations (1-10 ug/l) but can be toxic when present in abnormally high concentrations. In order to better understand factors controlling concentration, the adsorption of several trace metals on a natural marine sediment in sea water was studied. This was part of a proposed long-range project to investigate the effects of sand and gravel ocean mining on the marine environment of Massachusetts Bay. It was expected that trace metals might be released to the water column from fines discharged during dredging. Thus, information was required regarding the rate and amount of adsorption of several trace metals onto suspended dredge spoils.

The -230 mesh portion of a sediment sample taken adjacent to the dredge area was obtained by wet screening with sea water since this sized material was expected to simulate the dredge spoils. This material was used for trace metal adsorption experiments. Total and HCl extractable metal

(major and minor) concentrations, cation exchange capacity, organic matter content, mineralogical characterization, and other parameters were determined as an aid in interpreting adsorption behavior.

A 2<sup>3</sup> factorial laboratory experiment was designed to investigate the adsorption of 100 ug/l of added Cu, Pb, Zn, Cd, Ni, and Co on -230 mesh sediment in sea water. High and low levels of temperature, oxygen concentration, and light were employed as independent variables, since these factors were known to differ between the ocean floor and at the water surface. Due to the method of manipulating oxygen levels, pH also varied and this was found to have a much greater influence than oxygen concentration.

All dissolved metal concentrations were monitored by a combined solvent extraction-atomic absorption procedure. In preliminary experiments the extent of adsorption was investigated up to six days. Since the major changes occurred rapidly, the rate of adsorption was studied by determining the dissolved metal concentrations at frequent intervals for times up to three hours. The concentration of dissolved metals after three hours of equilibration was used to estimate the effects of these environmental factors on the degree of adsorption.

In general, most of the spiked Cu and Pb were adsorbed almost immediately under all experimental conditions employed. The other metals were adsorbed more slowly with a greater part of the adsorption occurring in the first thirty minutes. Zn and Cd showed very strong adsorption at the end of three hours at 20°C and moderate adsorption at 4°C. Co and Ni were adsorbed to a much lesser extent than the other metals under all experimental conditions.

Since adsorption behavior on sediments and assimilation

by living organisms varies with metal speciation, a copper specific ion electrode was used for estimating total and ionic concentrations in sea water. In addition, the electrode was to be used in monitoring ionic copper concentrations in the adsorption experiments. Known addition methods for determining total copper concentrations in sea water compared favorably with the solvent extraction-atomic absorption method indicating that this electrode can be used for precise measurements. The concentration of free cupric ion in sea water was estimated at 0.001 ug/l which is approximately 0.05% of the total (2.2 ug/l) copper.

The presence of organic matter normally found in sea water was shown to complex some of the copper. Extraction of part of the organic matter resulted in a threefold increase in the amount of ionic copper for added copper concentrations up to 500 ug/l. However, this still represented an extremely low percentage of  $\text{Cu}^{2+}$ .

From earlier thermodynamic studies, it was predicted that the relative proportions of copper inorganic complexes in sea water were pH dependent, and that at pH 8.1 the major specie was  $\text{Cu}(\text{OH})_2^\circ$ . This dependency was verified by measuring the concentration of  $\text{Cu}^{2+}$  as a function of pH for a sea water sample spiked with 200 ug/l of copper. It was found that the ionic copper content decreased as the pH was raised from 7 to 9 due to the formation of  $\text{Cu}(\text{OH})_2^\circ$ .

Because of the influence of these variables, the very low  $\text{Cu}^{2+}$  concentration, and the slow electrode response, continuous in situ monitoring of the adsorption studies was not possible.

## INTRODUCTION AND PURPOSE OF EXPERIMENT

In 1971, the United States produced 987 million tons of sand and gravel aggregate valued at 1.2 billion dollars.<sup>1</sup> With the exception of a few very minor operations in bays, tidal rivers, and estuaries, the source of this aggregate was from land-based operations. Because the major uses of this sand and gravel aggregate are for highway and street construction as well as building construction and maintenance, it is presently predicted that, by the year 2000, the demand for sand and gravel will increase by 20% annually. The present land-based reserves of acceptable quality and within economical transportation distances of major population centers are estimated at no more than 15 years. For example, half the towns in Connecticut now have no usable nearby source of sand. In addition, there is increasing public concern with the environmental aspects of sand and gravel operations near residential areas due to problems with noise, dust, and water pollution.

It has been established by the U. S. Corps of Engineers that deposits of as much as 6 billion tons of sand and gravel lie within several miles of the coastline on the northern Continental Shelf of the United States. These deposits, which originated from glacial activity, are generally found in water less than 100 feet deep. The economic viability of offshore mining of sand and gravel has been established in the United Kingdom where such mining has been conducted since 1929. Unfortunately, they have not conducted any integrated environmental study, concentrating their efforts almost exclusively on relationships between mining and beach erosion. Therefore,

little factual data exists for use in predicting the potential ecological impacts of offshore mining operations.

A recent survey by the Battelle Memorial Institute<sup>1</sup> indicated that most environmental research on the effects of dredging has been concentrated in fresh and brackish waters. Silt and clay from channel dredging may cause considerable damage to fish and other aquatic organisms. It is very difficult, however, to extrapolate this research to offshore waters where sediments are different from fresh and brackish waters, marine organisms are different, and the tides and currents which will affect particle settling rates are different. In view of this paucity of data concerning the environmental impact of offshore mining, there has been little effort at large-scale operation in the United States and many legal and de facto moratoriums at various levels of government have appeared.

The New England Offshore Mining Environmental Study (Project NOMES) was an experiment designed to evaluate the long-range, direct and indirect ecological effects of offshore sand and gravel mining. The experiment was to involve numerous laboratory studies and a carefully-controlled, short-duration dredging of an area in Massachusetts Bay. Extensive sampling and laboratory analyses were to be associated with the pre- and post-dredging periods in both the dredge site and the adjacent impact area where dredge spoils were expected to redeposit. It was hoped that this study would provide a scientific base for the establishment of realistic safeguards over potential future offshore mining operations.

The proposed mechanism of dredging involved a system analogous to a giant vacuum cleaner mounted on a barge. The sand, gravel, and associated fine sediments from the dredge site would be retained onboard the barge in settling tanks for



brief periods after which the suspended fines would be discharged overboard. Engineering estimates indicated that the maximum probable particle size of fines to be discharged would be approximately 62  $\mu\text{m}$  (-230 mesh). Depending on their size and density, the particles would gradually settle in the water column to the sea floor beneath. Settling time could be quite long due to the turbulence in the area. Since these fines, especially the clay-sized material ( $< 2 \mu\text{m}$ ), have substantial active surface area, adsorption and/or desorption could substantially alter the concentration of dissolved species in the water column. Information on this question was of considerable interest.

The total ecosystem involved in this experiment consists of four major elements: (a) the sea bed in the dredge site, (b) the sea bed in the silt impact area, (c) the marine life inhabiting both the water column and the sea floor, and (d) the atmosphere over the site. The dynamics of these subsystems are all interrelated; therefore, complex ecological effects may be expected from dredging. The generation of a comprehensive model will require intimate involvement of several interrelated disciplines in sample collection, sample analysis, and data interpretation stages.

The first phase of the chemical investigation was a comprehensive analysis of selected sediment core samples from the dredge site area. The characterization was required in order to assess the potential chemical impact of discharge of the dredge spoils. The second phase was a laboratory investigation of adsorption-desorption behavior of trace metals on typical fine sediment from the dredge area. These studies incorporated estimates of the effects of environmental factors such as temperature, light level, and oxygen concentration which were expected to vary widely between the sea floor and the ocean surface.

## LITERATURE REVIEW

### Trace Metals in Sea Water

The fourteen most abundant elements in sea water are O, H, Cl, Na, Mg, S, Ca, K, Br, C, Sr, B, Si, and F.<sup>2</sup> All of these have concentrations in sea water greater than one mg/l. The remaining elements are present at concentrations ranging down to less than a ug/l and are generally classed as the minor or trace elements. In fact, some of the elements in the list, such as Sr, B, and F, are also considered trace elements. The important point is that very small concentrations of a large number of these elements play important roles in the inorganic and biochemical reactions which occur in the marine environment.

Several trace metals can be essential to living organisms at some minimum concentration and at the same time, be toxic at a higher concentration.<sup>3</sup> Other trace metals, not known to be essential, may also be toxic at abnormally high concentrations. Copper is an example of an element which is essential for the growth of certain algae. It is also found in other marine plant life and is generally believed to increase the stability of chloroplasts. One of the best known occurrences of copper is in hemocyanin, the respiratory pigment in many marine invertebrates such as the lobster. It is also required in the formation of melanin. The concentration of copper required for each of these essential functions is in the ug/l concentration range. In contrast, higher concentrations of copper in the form of the sulfate have been used for algae growth control. Copper compounds are commonly used as the toxic active ingredient in

marine antifouling paints. This contrast in behavior at different concentration levels is not unique to copper.

One important role of trace metals is enzyme catalysis.<sup>4</sup> Manganese, copper, zinc, and cobalt are four elements which have been widely studied because of their involvement in enzymatic reactions. In some cases, these metals can be replaced by other metals when the latter are present in abnormal concentrations. A loss of the enzyme's catalytic function may occur. Cadmium is an example of a trace metal which is known to inhibit several mammalian enzymes.

The functional properties of trace metals in sea water are very much dependent on the particular species present. Certainly, one would expect a difference in reactivity and metabolic assimilation for the ionic form of an element in contrast to a metallo-organic complex. Mercury is a case in point. Organic mercury (methyl mercury) is much more toxic than any of the inorganic forms. Likewise, copper, found as a pollutant in surface fresh water, can be toxic to fish. This toxicity, however, is dependent upon the different soluble forms of copper present in the water, the ionic species being the most toxic. The toxicity of cyanide solutions to fish can be reduced if copper is present. This is due to the formation of copper cyanide complexes which are relatively nontoxic. Hence, the determination of total concentrations of trace metals without regard to speciation does not provide the physiologist or the toxicologist with adequate information. Attention to this important aspect of trace metals is in the early stages of development.

### Speciation in Sea Water

There have been two principal approaches in determining the speciation of dissolved metals in sea water. One approach is based on equilibrium calculations using thermodynamic data available in the literature to estimate the concentrations of free metals. The other approach is based on experimental techniques to directly or indirectly determine the concentrations of free ions in solution. For these measurements, the sodium, potassium, calcium, magnesium, and copper specific ion electrodes have been used. Other electro-analytical techniques such as voltammetry have also been employed.<sup>5</sup> Whenever possible, correlation of mathematical models based on thermodynamic calculations with experimental determinations is attempted. At present, however, experimental values especially for trace metals are often unavailable.

Most mathematical models of speciation have focused on the major ions in sea water, probably because the necessary thermodynamic data are more readily available for these ions. In a comprehensive theoretical study, Garrels and Thompson<sup>6</sup> calculated the distribution of the major dissolved species in sea water. Using thermodynamic dissociation constants and individual ion activity coefficients from their own work as well as other literature values, they estimated the concentrations of species formed between  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . No consideration was given to chloride complexes since there is no evidence for ion-pair formation with these four metals. All calculations assumed a temperature of 25°C and one atmosphere total pressure. First, mass balance equations were written for each constituent. Then, substitution of the dissociation constants for each of the

species in terms of activities made it possible to write several independent mathematical expressions which could be solved simultaneously.

The general picture which emerged from this mathematical treatment was that the major cations in sea water exist chiefly as uncomplexed species. Essentially all of the sodium and potassium, and about 85-90% of the calcium and magnesium are present as free ions. In contrast, the anions, except for chloride, are strongly complexed. Most of the carbonate, approximately one third of the bicarbonate, and nearly half the sulfate are paired with various cations. A summary of these and other data is shown in Table 1.

The calculations made by Garrels and Thompson are very much dependent on the reliability of the activity coefficients employed. Support for the correctness of the values they used may be found in the work of Berner<sup>7</sup>, who accurately measured the pH of sea water samples, which were previously equilibrated with calcite and aragonite at known partial pressures of carbon dioxide. The calculated activity coefficients of bicarbonate, carbonate, and calcium ions agreed closely with those of Garrels and Thompson.

Hanor<sup>8</sup> developed a computer program to calculate the distributions of all species of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{Cl}^-$  in sea water. His model was similar to Garrels' and Thompson's but employed extended Debye-Hückel power functions to calculate activity coefficients for charged species. Results (Table 1) are in substantial agreement with the other values shown. Similar work by Kestor and Pytkowicz<sup>9</sup> led to comparable results (Table 1). Pytkowicz and Gates<sup>10</sup> also obtained an estimate of the free magnesium ion concentration from solubility

TABLE 1

DISTRIBUTION OF THE MAJOR IONS IN SEA WATER  
(25°C, 19‰ Chlorinity, pH 8.1)

Ion	% Free (Calculated)	% Free (Exp't)	% Me-SO <sub>4</sub>	% Me-HCO <sub>3</sub>	% Me-CO <sub>3</sub>
Ca <sup>2+</sup>	91 ( 6)	86.3 ( 9)	8 ( 6)	1 ( 6)	0.2 ( 6)
	88.5 ( 9)	84 (13)	10.8 ( 9)	0.6 ( 9)	0.07 ( 9)
	91.5 ( 8)		7.6 ( 8)	0.7 ( 8)	0.2 ( 8)
Mg <sup>2+</sup>	87 ( 6)	88.1 ( 9)	11 ( 6)	1 ( 6)	0.3 ( 6)
	89 ( 9)	90 (12)	10.3 ( 9)	0.6 ( 9)	0.13 ( 9)
	89.9 ( 8)		9.2 ( 8)	0.6 ( 8)	0.3 ( 8)
	90 (11)		9.2 (11)		
	90 (10)		10. (10)		
Na <sup>+</sup>	99 ( 6)	97.1 ( 9)	1.2 ( 6)	0.01 ( 6)	0.0 ( 8)
	97.7 ( 9)		2.2 ( 9)	0.03 ( 9)	
	99.0 ( 8)		1.0 ( 8)	0.0 ( 8)	
K <sup>+</sup>	99 ( 6)		1 ( 6)	0.0 ( 8)	0.0 ( 8)
	98.8 ( 9)		1.2 ( 9)		
	98.5 ( 8)		1.5 ( 8)		
Sr <sup>2+</sup>	94.9 ( 8)		4.6 ( 8)	0.4 ( 8)	0.1 ( 8)
Ba <sup>2+</sup>	93.2 ( 8)		6.5 ( 8)	0.2 ( 8)	0.0 ( 8)

	Free % Ion (calc)	% Ca-A	% Mg-A	% Na-A	% K-A	% Sr-A % Ba-A
SO <sub>4</sub> <sup>2-</sup>	54 (6)	3 (6)	21.5 ( 6)	21 (6)	0.5 (6)	0.0 (8)
	39 (9)	4 (9)	19.4 ( 9)	37.2 (9)	0.4 (9)	0.0 (8)
	62.9 (8)	2.8 (8)	17.4 ( 8)	16.4 (8)	0.5 (8)	
			17.5 (11)			
HCO <sub>3</sub> <sup>-</sup>	69 (6)	4 (6)	19 ( 6)	8 (6)	0.0 (8)	0.0 (8)
	70 (9)	3.3 (9)	17.8 ( 9)	8.6 (9)		0.0 (8)
	74.0 (8)	3.2 (8)	14.4 ( 8)	8.3 (8)		
CO <sub>3</sub> <sup>2-</sup>	9 (6)	7 (6)	67 ( 6)	17 (6)	0.0 (8)	0.0 (8)
	9.1 (9)	6.4 (9)	67.3 ( 9)	17.3 (9)		0.0 (8)
	10.2 (8)	7.1 (8)	63.2 ( 8)	19.4 (8)		

Me represents the appropriate cation.

A represents the appropriate anion.

equilibria of magnesium hydroxide (brucite) and potentiometric pH measurements. Fisher<sup>11</sup> employed a unique approach based on ultrasonic absorption to estimate the percentage of the free magnesium ion in sea water.

Direct estimates of magnesium ion concentrations<sup>12</sup> and calcium ion concentrations<sup>13</sup> have been made using specific ion electrodes. The calibrating solutions contained known varying concentrations of magnesium and calcium in a matrix of metal chloride salts at concentrations comparable to sea water. Since chloride ion shows no complexing ability with the major cations, electrode measurements could be validly employed. It was estimated that 84% of the calcium in sea water existed as the free calcium ion, which is in fair agreement with the other values reported from mathematical models (Table 1). For magnesium, the electrode determination resulted in an estimation that 90% of the total magnesium existed as the free ion which is in good agreement with the calculated values.

The usefulness of specific ion electrodes in speciation research seems clearly established. As more electrodes become available, more research will undoubtedly be undertaken. For example, fluoride in sea water<sup>14</sup> has already been estimated to be approximately 50% complexed by magnesium as the ion-pair  $\text{MgF}^+$ .

Copper is an example of a trace metal which several researchers have investigated while attempting to obtain reliable information on total concentration and the degree of complexation. For example, Corcoran and Alexander<sup>15,16</sup> compared what they called ionic versus total copper in sea water samples using neocuproine to complex the copper before and after perchloric acid digestion. The copper neocuproine complex was measured spectrophotometrically. The authors concluded that there was a higher percentage of copper present

as organic complexes than as ionic copper. However, it should be recognized that there is an inherent danger in this procedure due to the potential for contamination from reagents and apparatus used in the digestion procedure. Furthermore, it is difficult to rationalize the presence of soluble copper complexes with stability constants greater than that for copper neocuproine [ $K_{stab} = 10^{19}$ ]<sup>17</sup> except in limited amounts. Certainly, this procedure cannot provide a reliable distinction between ionic and complexed copper.

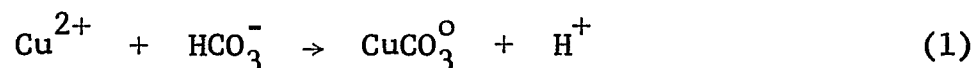
Corcoran and Alexander<sup>15</sup> also studied the distribution of trace metal species as a function of depth in the tropical waters of Florida. They determined iron, nickel, and copper concentrations at depths up to 600 meters and concluded that iron existed primarily as particulate and soluble complexes in approximately a 1 to 1 ratio, while copper was present primarily as soluble organic complexes. All three micronutrients showed maximum total concentrations near depths of 300 to 600 meters. Since acid digestion was again used in conjunction with complexing agents to distinguish between ionic and complexed forms of metals, the same reservations expressed earlier apply.

Additional evidence to show that copper-organic compounds are present in sea water was obtained by Slowey, Jeffrey, and Hood<sup>18</sup>, who used a nonpolar solvent to extract these complexes. They suggested that copper was probably associated with phospho-lipids, amino-lipids, or the porphyrin fraction of the extractable organic material. No experimental evidence was offered to verify the presence of these specific complexes but they did find appreciable non-dialyzable copper. They also obtained results in general agreement with those of Corcoran and Alexander<sup>15</sup> using persulfuric acid digestion.



An alternate approach using high-energy, ultra-violet light to destroy the organic matter was employed by Williams.<sup>19</sup> He also found higher copper values in the samples after the ultraviolet light treatment. Since this method is less prone to contamination problems, the results seem to provide stronger evidence for the presence of copper-organic complexes.

Stiff<sup>20</sup> studied the speciation of copper in a bicarbonate system using a specific ion electrode. The electrode was first used to experimentally determine the equilibrium constant for the reaction



and to verify the non-existence of the  $\text{CuHCO}_3^+$  species by graphical analyses. The electrode was then used to estimate the concentration of uncomplexed copper in bicarbonate solutions of varying concentrations. For example, at pH 7.5 with a bicarbonate concentration of  $1 \times 10^{-3}$  M, 11% of the total copper was estimated to be in the ionic form; while at pH 8 and a bicarbonate concentration of  $5 \times 10^{-3}$  M, only 0.9% was in the ionic form. In this paper, it was shown that soluble copper consists only of neutral copper carbonate and free ionic copper. However, no mention was made of  $\text{Cu}(\text{OH})_2^0$  species or of any organic complexes.

To determine the chemical forms of copper in sea water and the total copper concentration, Odier and Plichon<sup>21</sup> utilized AC polarography. The shift of the reduction half-wave potential of copper, which depends on the concentrations of individual ligands and on the pH, made it possible to establish the formula and the formation constant of each copper complex. The major forms of copper, according to these

authors, were  $\text{Cu}^{2+}$ ,  $\text{CuCl}^+$ , and  $[\text{Cu}(\text{HCO}_3)_2(\text{OH})]^-$ .

Mathematical models have also been used to study speciation of trace metals. Goldberg<sup>22</sup> calculated the speciation of copper in sea water under the assumption that chloride was the only ligand in equilibrium with the solvated copper ion. He concluded that 65% of the copper existed as  $\text{Cu}^{2+}$ , 29% as  $\text{CuCl}^+$ , and 4% as  $\text{CuCl}_2^0$ . The remaining 2% existed as  $\text{CuCl}_3^-$  and  $\text{CuCl}_4^{2-}$ .

In another study, Goldberg<sup>2</sup> suggested that the model of Garrels and Thompson<sup>6</sup> could be applied to trace elements in sea water. As an example, he calculated the degree of interaction between  $\text{Cd}^{2+}$  and the anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{OH}^-$  under the assumption that interaction between the ions resulted only in the formation of mono-ligand complexes. He neglected such species as  $\text{CdCl}_2^0$  and  $\text{CdCl}_3^-$ . Using this oversimplification, he calculated that 83% of the cadmium existed as  $\text{CdCl}^+$ , 16% as  $\text{Cd}^{2+}$ , and 1% as  $\text{CdSO}_4^0$ .

A more comprehensive study using the same general approach was reported by Zirino and Yamamoto.<sup>23</sup> They estimated the extent of complexation of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  with  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in sea water. For each metal considered, the best available estimates of ion activity coefficients and stability constants were used to calculate the concentrations of uncomplexed metal ion, and the various complexed species as percentages of the total metal concentration. The metals were considered to be in the divalent state, and interactions between a cation and anion were assumed to result only in the formation of mono, di, tri, and tetra-ligand complexes. Polynuclear complexes such as  $\text{Cu}_2(\text{OH})_2^{2+}$  and organic complexes were excluded from their model, primarily due to the lack of required stability constant data. All calculations were made for sea water of

19 parts per thousand chlorinity, at 25°C and one atmosphere total pressure. Thermodynamic equilibrium was assumed. The results for the chemical speciation of copper, zinc, cadmium, and lead are summarized in Table 2 for pH 8.1. The effect of pH is also presented in the paper.

Chromium speciation in sea water has been studied using thermodynamic calculations by Elderfield.<sup>24</sup> This analysis was accomplished by collecting all pertinent equilibrium expressions and solving them simultaneously. However, since all the expressions involving chromium are not known, the results obtained can only be used as an approximation. Based on this study, the author concluded that chromium exists primarily as hydroxy and chromate complexes in sea water.

At present, direct experimental evidence is too limited to permit objective comparisons with the results of thermodynamic calculations. However, as a generalization, it seems unlikely that agreement between the mathematical models and experimental measurements will be as good for trace metals as for the major constituents. The primary reason for this belief resides in the fact that concentrations of one to two mg/l of organic matter are common in sea water, and these constituents will exert a major influence on trace metals present at the ug/l concentration level. In contrast, the presence of organic matter will have little influence on complexation of major cations. Therefore, as long as organic ligands cannot be included in thermodynamic estimates, it is difficult to see how these mathematical models can be reliable predictors of speciation for trace metals.

TABLE 2

CHEMICAL SPECIATION OF SEA WATER<sup>1.</sup>  
(25°C, 19‰ Chlorinity, pH 8.1)

Copper		Zinc		Cadmium		Lead	
Species	% of Total	Species	% of Total	Species	% of Total	Species	% of Total
$\text{Cu(OH)}_2^0$	90	$\text{Zn(OH)}_2^0$	62	$\text{CdCl}_2^0$	51	$\text{PbCO}_3^0$	80
$\text{CuCO}_3^0$	8	$\text{Zn}^{2+}$	17	$\text{CdCl}^+$	39	$\text{PbCl}^+$	10
$\text{Cu}^{2+}$	1	$\text{ZnCl}^+$	6.4	$\text{CdCl}_3^-$	6	$\text{PbCl}_2^0$	4
$\text{CuOH}^+$		$\text{ZnCO}_3^0$	5.8	$\text{Cd}^{2+}$	2.5	$\text{Pb}^{2+}$	1.5
$\text{CuSO}_4^0$		$\text{ZnSO}_4^0$	4	$\text{CdSO}_4^0$		$\text{PbCl}_3^-$	1.5
$\text{CuHCO}_3^+$		$\text{ZnCl}_2^0$	4	$\text{CdCO}_3^0$		$\text{PbSO}_4^0$	
$\text{CuCl}^+$	1	$\text{ZnCl}_3^-$			1	$\text{PbCl}_4^{2-}$	
$\text{Cu(CO}_3)_2^{2-}$		$\text{ZnHCO}_3^+$		$\text{CdHCO}_3^+$			1
$\text{CuCl}_2^0$		$\text{ZnCl}_4^{2-}$	1	$\text{CdOH}^+$		$\text{PbHCO}_3^-$	
		$\text{ZnOH}^+$				$\text{PbOH}^+$	

1. Adapted from<sup>23</sup>.

### Analytical Measurements in Sea Water

Riley and Chester<sup>25</sup> have suggested the subdivision of sea water into four major categories: (a) particulates, (b) dissolved species, (c) colloids, and (d) organically bound trace metals. While this subdivision is quite arbitrary, it is a classification scheme which has been widely adopted.

The suspended particulate matter in sea water is generally defined as that material which does not pass a 0.45  $\mu\text{m}$  filter. A recent study by Wagemann and Brunskill<sup>26</sup> revealed one of the fallacies of this system. These authors studied the effectiveness of filtration with two different types of membrane filters of the same nominal pore size. They found that there were major differences in particulate retention for aliquots of the same samples using silver metal (Selas Flotronics) and cellulose ester (Millipore Filter Corp.) filters. Not only was the overall retention different but it also varied from element to element in a complex fashion which the authors were unable to explain.

The suspended particulate matter of sea water is highly variable in both composition and amount. The inorganic fraction consists mainly of minerals such as feldspars, clays, and quartz formed by the weathering of terrestrial rocks. Other inorganic species often present are the siliceous and calcareous remains of dead organisms. The organic particulate fraction is derived from the decomposition and metabolic products of living organisms. In general, the waters of open oceans away from the continental shelf and at depths greater than 200 meters contain only small amounts of suspended particulates, which are generally low in organic content. Typically, the total concentration of particulates in such water

may range from 0.5 to 250 ug/l with an average of approximately 40 ug/l. In contrast, coastal waters which are subject to major additions from rivers and other man-made sources tend to contain much higher total concentrations of particulates and also correspondingly higher concentrations of organic matter.

The dissolved inorganic species present in sea water are principally electrolytes, although uncharged species such as boric acid and dissolved gases are included in this category. The multitude of possible soluble complexes of both major and minor ions has been discussed in the previous section on speciation.

At the natural pH of sea water, a considerable number of polyvalent ions such as  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Zr}^{4+}$ , and  $\text{Th}^{4+}$  are slowly hydrolyzed to form colloidal hydroxy compounds which may eventually coalesce and precipitate. Of these,  $\text{Fe}^{3+}$  has been most widely studied because of its biological importance; but investigations to date have been hindered due to its very low concentration.

Ocean water generally contains very low concentrations of dissolved organic compounds such as humic and amino acids, although local coastal areas may contain concentrations of 10 or more mg/l. This organic matter is effective in forming a wide variety of complexes with metals. While these concentrations are relatively insignificant with respect to the major cations, metallo-organic complexes may very well represent a high percentage of the total concentration of several trace metals.

With such a complex and variable system, representative sampling presents a formidable problem. The high salt content of the medium greatly restricts materials which can be used in sampling. A suitable water sampling device must

not contribute contaminants to the sample. Therefore, in investigations of trace metals, metallic devices are unsatisfactory. Even plastic-coated samplers such as the epoxy-coated Knudsen-Nielsen bottles, used by Alexander and Corcoran<sup>15</sup>, allowed contamination due to cracks in the epoxy, which permitted contact of the sea water with the bronze walls of the sample bottles. These authors found it necessary to employ a sampling device constructed of polyvinyl chloride with a minimum of external stainless steel fittings. Needless to say, pressure considerations for deep water sampling impose restrictions on all plastic devices.

Once samples have been secured, analyses should be performed immediately to avoid changes resulting from continued biological activity and adsorption-desorption phenomena on the container walls. However, oftentimes, this is impractical and in such cases, special procedures must be employed to store the samples. Freezing<sup>27</sup> in polyethylene bottles has been recommended. When deep freeze facilities are not available, it is possible to preserve sea water samples for up to one month by chemical stabilization, such as acidification to a pH of approximately one. When samples are not frozen, high density polyethylene bottles should be used to avoid the loss of water vapor.

Several mechanisms can contribute to alteration of the concentration of dissolved trace metals. One form of contamination is the liberation of metal from particulate matter as a result of either desorption or decomposition. Trace metals can also be acquired from storage vessels such as polyethylene which always contain variable amounts of metallic impurities introduced during the manufacture of the plastic. It is good general procedure to clean all plastic and glass containers with complexing agents and/or strong acid. It is also necessary

to be conscious of the possibility of loss of trace metals by adsorption on suspended particulates and the walls of the storage containers.

Sample preparation for chemical analysis generally requires the use of numerous reagents, apparatus, and materials, all of which are potential sources of contamination. Consequently, it is usually necessary to purify even high-purity chemicals before they are employed in trace metal determinations. Such purification may be accomplished by a variety of techniques such as chelating ion exchange resins, solvent extraction, or electrolysis as used in anodic stripping voltammetry. Robertson<sup>28</sup> conducted a study of the potential sources of contamination normally encountered in trace metal analysis of sea water. As examples of some of the rather surprising findings, it was reported that Kimwipes (Kimberly-Clark Corp.) contained approximately 49 parts per million (ppm) zinc and Millipore filters contained an average of 2.4 ppm zinc and over 17 ppm chromium. Polyvinyl chloride contained 0.63 ppm copper. When we recall that sea water contains these elements at concentrations in the ug/l range, (approximately equivalent to parts per billion (ppb)), the significance of these levels of contaminants becomes obvious. Of course, the above values given by Robertson represent total concentrations contained in these materials and does not necessarily represent the amount of contamination that would potentially be added to a sample during the course of normal use of these materials.

Numerous analytical methods have been used for the determination of trace metals in sea water. Riley<sup>29</sup> and Joyner, et al.<sup>30</sup> have reviewed some of the most commonly used methods. Neutron activation, isotope dilution analysis, and atomic absorption-flame emission spectroscopy lead the list,



although there have been many applications of ultraviolet-visible absorption spectrophotometry, various polarographic methods, optical emission spectroscopy, X-ray emission spectroscopy, and spark source mass spectroscopy.

For the vast majority of trace metal determinations in sea water, some means of preconcentration is employed. Of the many techniques available, solvent extraction of metal complexes is most frequently used. Since atomic absorption-flame emission procedures are readily adaptable to a number of nonaqueous solvents, the combination of solvent extraction and atomic absorption-flame emission has been a natural one. In this area, the use of ammonium pyrrolidine carbodithioate (APCD) has been widely used because it is effective in complexing a very large number of metals over a pH range of 2 to 8. (In most literature references, this compound has been erroneously called ammonium pyrrolidine dithiocarbamate -APDC). The solvent most frequently used to extract the metal APCD complexes is methyl isobutyl ketone (MIBK). This system has been used to determine ug/l amounts of Zn, Cu, Pb, Ni, Cd, Co,  $\text{Cr}^{6+}$ , Fe, and Mn in water samples by Paus<sup>31</sup>, Yamamoto et al.<sup>32</sup>, Schaller et al.<sup>33</sup>, Fishman and Midgett<sup>34</sup>, Brooks et al.<sup>35</sup>, and others. A radiotracer study of the extraction efficiency of this system was performed on the elements, Cu and Zn, by Koirttyohann and Wen<sup>36</sup>; they reported complete extraction throughout the pH range of 2 to 6. However, atomic absorption responses indicated less than 100% extraction in some cases and there was slight pH dependence. They recommended the addition of perchloric acid to the aqueous phase prior to pH adjustment as a means of overcoming this problem, although they could offer no explanation of how the perchlorate functioned.

Other solvent extraction systems have been used in

conjunction with atomic absorption to determine ug/l concentrations of trace metals in water. Iron and nickel were determined by chelation with 8-hydroxyquinoline and dimethylglyoxime respectively, followed by extraction into MIBK by Jones and Eddy<sup>37</sup> and by a double extraction with dimethylglyoxime.<sup>38</sup>

Several trace metals were determined in fresh water by Nix and Goodwin<sup>39</sup> and in sea water by Kuwata et al.<sup>40</sup>, both using sodium diethyl carbodithioate-MIBK. Kanke et al.<sup>41</sup> employed dithizone-nitrobenzene extraction coupled with atomic absorption spectrophotometry to determine ug/l levels of Cd, Zn, Pb, and Cu in water. Frei et al.<sup>42</sup> described procedures for the extraction of pyridine-2-aldehyde-2-quinolylhydrazone complexes of Cd, Co, Cu, Ni, and Zn into MIBK. Dithizone-benzene was used by Park<sup>43</sup> to extract lead and zinc from natural water prior to X-ray spectrographic measurements.

Riley and Taylor<sup>44</sup> demonstrated that commercially available chelating resins (Chelex 100, Bio-Red Laboratories) could be used for the concentration of trace metals from sea water. The adsorbed metals were eluted from the column with acid and analyzed by atomic absorption methods. Alternatively, instead of elution techniques, a pellet could be made from this resin and used for X-ray spectrographic analysis.<sup>45</sup>

A few attempts have been made to determine trace elements in water by atomic absorption without preconcentration. The direct determination of 12 trace metals in fresh water samples using a heated graphite furnace was described by Fernandez and Manning.<sup>46</sup> However, similar attempts by Segar et al.<sup>47</sup> to analyze sea water were relatively unsuccessful due to the extremely high background created by the vaporization of sodium chloride. They did find it possible to determine manganese and iron after first vaporizing the sodium chloride,

but there were some losses encountered in this approach. The sample boat technique was successfully used by Burrell and Wood<sup>48</sup> to directly determine total zinc in sea water. It should be remembered however, that the detection capability for zinc is greater than for most elements and, therefore, success with a broad spectrum of trace metals by this approach is unlikely. In another direct method for the determination of zinc in water, Marshall and Smith<sup>49</sup> used atomic fluorescence in conjunction with electrodeless discharge lamps.

Spectrophotometric measurements in both the ultra-violet and visible regions have been widely employed for trace metal determinations in water. One of the most frequently determined elements by this technique is copper. Akaiwa et al.<sup>50</sup> extracted copper from natural water with thenoyltrifluoroacetone in cyclohexane. Stiff<sup>51</sup> used neocuproine after nitric acid digestion to determine total copper and 3-propyl-5-hydroxy-5-D-arabionot-etrahydroxybutyl-3-thiazolidine-2-thione to determine free cupric ion and copper complexes with stability constants less than the cyanide complex. The latter reagent does not require extraction from the aqueous phase prior to spectrophotometric measurement. Copper in sea water was determined by Balabanoff et al.<sup>52</sup> by precipitation with lead diethylcarbodithioate. The precipitate was dissolved in chloroform, and the copper complex measured at 435 nm. Quinoline-2-aldehyde-2-quinolyldiazine was used by Abraham et al.<sup>53</sup> to form a benzene soluble copper complex for analysis in sea water. Lead in sea water was determined at 270 nm as the tetrachloro complex by Skurnik-Sarig et al.<sup>54</sup>. Cobalt was extracted from sea water with 1-nitroso-2-naphthol in chloroform, followed by spectrophotometric determination of the chelate by Kentner

and Zeitlin.<sup>55</sup>

New developments in electrochemical instruments during the past five years have greatly increased the popularity of this method for determining trace metals in fresh and saline water. Zinc was determined in sea water by Zirino and Healy<sup>56</sup> using pH controlled differential anodic stripping voltammetry (ASV) and later, they determined the concentrations of Zn, Cd, Pb, and Cu in both fresh and saline waters.<sup>57</sup> Abdullah and Royle<sup>58</sup> determined Cu, Pb, Cd, Ni, Zn, and Co in natural waters by pulse polarography after pre-concentrating with the chelating ion exchange resin Chelex 100. In a somewhat analogous fashion, Muzzarelli and Sipos<sup>59</sup> used ASV to demonstrate that chitosan can be used to collect naturally occurring Zn, Cd, Pb, and Cu from sea water. Additional work by these techniques can be expected in the future as a means of generating information on speciation.

Another system which is excellent for the determination of trace elements in sea water is neutron activation, but it is limited by the availability of thermal neutron sources with sufficient flux. Examples of the successful use of this approach are Krishnamoorthy et al.<sup>60</sup>, Adbullaev et al.<sup>61</sup>, and Matthews and Riley.<sup>62</sup>

Specific ion electrodes have a unique potential because both ionic and total concentrations of many metals can be estimated depending on the measurement technique employed. In general, these electrodes respond directly to the activity of a given ion even in complex solutions containing large excesses of other ions. This frequently allows measurements in natural fluids such as blood, sea water, and others, without sample pretreatment. They have also been widely touted as promising sensors for continuous monitoring especially in water systems. However, the sensitivity of the

electrode membranes to surface alteration by both dissolved and particulate materials has so far prevented a full realization of this goal.

Some common electrode materials are glass, crystalline solids, liquid ion exchangers, and a heterogeneous composition in which an inert binder such as silicone is used to contain crystalline solids. The most common electrodes are solid crystalline membranes and the liquid ion exchange type. According to Ross<sup>63</sup>, "A few crystalline materials are known which exhibit ionic conductivity at room temperature. In most cases, only one of the lattice ions is involved in the conduction process, usually the lattice ion with the smallest ionic radius and the smallest charge. Provided that the crystal is mechanically stable, chemically inert in the sample solution, and of low solubility, it can be used in the form of a thin section as an electrode membrane."

Since conduction proceeds by a lattice defect mechanism, the mobile ion must have size, shape, and charge distribution exactly similar to the vacancy in the crystal. Otherwise, the ion is excluded from the conduction process. Thus, if there are no chemical reactions at the crystal membrane surface, the device will behave in a Nernstian manner. In contrast, the selectivity of liquid membrane electrodes depends entirely on the ion-exchange process at the membrane surface.

Since the electrode used in this research was of the crystal type, discussion of interferences and related phenomena will be restricted to this type of electrode. Some of the main disadvantages of these electrodes are (a) a temperature-dependent response, (b) interferences due to reactions at the electrode surface, (c) difficulty in calibration for ionic measurements in highly complex matrices which limit the accuracy of these results, and (d) an increasingly slow response as

concentration decreases.

In most naturally occurring solutions containing trace metals, part of the metal will be present as free ions and part will be complexed. The concentration of free ions is related to the activity of these ions by

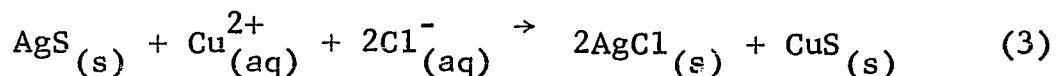
$$A = C \times \gamma \quad (2)$$

Activity coefficients,  $\gamma$ , can be estimated when total ionic strengths are known. Of course, in dilute solutions,  $\gamma$  approaches unity, but in solutions of high ionic strength, such as sea water where  $u = 0.70$ ,  $\gamma$  may be much less than 1. One method of compensating for activity coefficients is to synthesize standards in solutions of the same ionic strength as the samples.

Both single and mixed metal sulfide crystals have been synthesized for use as specific ion electrode membranes. An electrode using silver sulfide as the conducting crystal membrane has been shown to be responsive to both silver and sulfide ions.<sup>63</sup> Other mixed metal sulfides which have been found to make useful electrode membranes are copper, cadmium, and lead, all of which give Nernstian calibration curves. The mixed cupric-silver sulfide membrane is employed for measurements of cupric ion concentrations.

Because of the stringent requirements regarding size and charge of the mobile ion species in a crystal lattice, interference resulting from lattice penetration is not generally expected. However, Nernstian response in a solid membrane device assumes that all of the solid phase of the membrane is in equilibrium with the sample solution. This is not the case if there are species present in the sample solution which can react with components of the membrane. A

typical example of such an interference which results in the formation of a new solid phase is found with the mixed cupric-silver sulfide membrane when it is immersed in samples containing both cupric and chloride ions.



This interference is dependent on the concentration of chloride relative to the concentration of cupric ion in the sample and occurs only if the product  $[\text{Cu}^{2+}][\text{Cl}^{-}]^2$  exceeds  $1.6 \times 10^{-6}$ .<sup>64</sup> For 35 parts per thousand (ppt) sea water, the chloride concentration is 0.55M. Therefore, the maximum  $\text{Cu}^{2+}$  concentration which will not interfere with electrode operation in sea water is  $5.3 \times 10^{-6}$  M or approximately 340 ug/l. Since this is far in excess of the expected concentration of cupric ion in sea water, it should be possible to use the electrode without encountering this interference.

Fortunately, an electrode is not irreversibly harmed if it is inadvertently placed in a solution which results in the formation of a new solid phase. The reactions giving rise to the interferences are reversible, and the electrode can be restored to normal operation by exposure to high concentration of an appropriate reagent. If a copper electrode is poisoned by chloride ion as described in the previous paragraph, aqueous ammonia is effective in removing the precipitated silver chloride by forming the soluble diammine silver complex. Alternatively, the crystal membrane surface can be restored by gentle polishing on a very fine abrasive surface.

The direct measurement of hydrated cupric ion in sea water is complicated by the high ionic strength of the matrix, which make activity coefficient corrections difficult, and the extremely low concentration of the analyte. One approach

however, is to use aqueous standards and to approximate the correction by employing a salt with a noncomplexing anion, such as nitrate, at an ionic strength equivalent to sea water. Potassium nitrate can be used for this purpose. Rigid pH control is not essential. With carbon dioxide free water the concentration of hydroxide ( $1 \times 10^{-7} \text{M}$ ) is insufficient to affect significant complexation. If standards are made with cupric ion at the mg/l concentration level, equivalent to approximately  $1 \times 10^{-5} \text{M}$ , the loss of ionic copper due to hydroxide complexation would still be negligible.

At least three approaches can be used in making standards. One method is to use cupric ion concentrations much greater than those found in natural sea water in order to give faster electrode responses and to reduce the effect of contamination from the potassium nitrate which always contains small amounts of copper. The disadvantage of this procedure is that it requires extrapolation of the calibration curve three orders of magnitude in order to measure natural levels of cupric ion in sea water. Thus, any slight change in the slope of the calibration curve could cause large errors in the analysis of real samples. Nevertheless, this procedure has been used by Stiff<sup>51</sup> in fresh water where she actually extended her calibration curve four orders of magnitude.

Alternatively, standards can be made with the copper concentration in the ug/l concentration range but a severe contamination problem from the potassium nitrate then exists. Even if ultrapure potassium nitrate were used, the standards would not be stable for substantial periods due to adsorption on container walls. Complexation by hydroxide also exerts a significant effect at this copper concentration. In addition, slow electrode response would exist although there are graphical techniques for minimizing this difficulty.



A third an even more complicated alternative would require the preparation of synthetic sea water from ultra-pure reagents. This matrix would have the advantage of more closely matching standards with samples to be analyzed although organic complexing agents would most likely be omitted due to lack of adequate knowledge of their chemical composition in real sea water samples. Clearly, the advantages would be more than offset by the nearly insurmountable difficulties associated with reagent purification and standard storage.

In contrast to the difficulties encountered in the determination of ionic copper, total copper is more easily determined using the known addition method (also called the spike or known increment technique). Quite simply, the method consists of recording observed changes in electrode potential as a function of incremental additions of the analyte. The tacit assumption is made that the extent of complexation for the added increments is the same as for the concentrations originally present. The solution added should have a concentration 300 to 500 times the expected analyte concentration to avoid dilution errors, and should change the original concentration by a factor of 2 to 5 to insure adequate measurement precision for the change in potential. One or several increments may be added. When a single increment is used, the original concentration can be read directly from the "known increment scale" on a specific ion meter. Alternatively, greater precision can be obtained by adding several increments and constructing a Gran's plot on special volume corrected, semi-antilogarithmic paper (Orion Research, Inc.). The total copper concentration is calculated by extrapolating the best fitting straight line to the negative side of the horizontal axis. The procedure assumes a Nernstian slope of 29.6 mV. If the electrode exhibits a slope different from this value,

a blank must be employed. In the presence of complexing agents and without the use of a calibration curve, the known addition technique is the only procedure available for determining total concentration using ion selective electrodes.

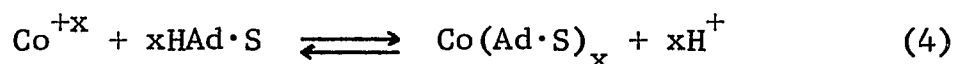
### Soluble Trace Metal-Particulate Interactions

The concentrations of dissolved trace metal species in sea water are greatly affected by interactions with suspended particulates and sediment. Despite the importance of these interactions, there has been a limited amount of research directly concerned with trace metal equilibria in marine environments. In contrast there is a large body of information concerning the interaction of soluble forms of trace metals in soils because of its importance in plant and animal nutrition. Since marine sediments are similar in chemical composition to soils, it appears appropriate to briefly consider some of the literature of soil chemistry. Principles enunciated in these works may, with some modification, be related to the marine environment.

It is generally accepted that trace metals such as Cu, Co, Ni, Zn, Pb, and others, form stronger bonds with clay minerals and humic acids present in soil than do the more predominant metals such as Ca, Mg, Na and K. DeMumbrum and Jackson<sup>65</sup> investigated the exchange reaction mechanism of copper and zinc with clays and peat using infrared absorption spectrophotometry. They reported that copper and zinc saturated clays caused a decrease of the hydroxyl absorption intensity for montmorillonite, vermiculite, and kaolinite. They explained this loss in intensity by copper or zinc replacement of hydrogen from structural OH groups of the clays. In the peat fractions, copper and zinc saturation produced

numerous shifts in the double bond region of the spectrum which were indicative of bonding with carbonyl and nitrosyl groups. Hodgson et al.<sup>66</sup> contested the simple ion exchange mechanism proposed by DeMumbrum and Jackson. In experiments using radioactive cobalt, evidence was obtained which was supported by theoretical calculations that hydrolysis of the metal cation occurred prior to adsorption of the hydroxy complex onto the clay. The possibility remains, however, that both the hydrolysis and the exchange mechanisms are active simultaneously.

Support for this latter contention is derived from a consideration of the work of Kurbatov et al.<sup>67</sup> who studied the isothermal adsorption of radioactive cobalt onto hydrous ferric oxide. Their experimental results could be explained by application of the mass law as shown in the following equations, in which HAd·S represents the hydrogen form of the



$$\text{K}_{\text{eq}} = \frac{[\text{Co}(\text{Ad}\cdot\text{S})_x] [\text{H}^+]^x}{[\text{Co}^{+x}] [\text{HAd}\cdot\text{S}]^x} \quad (5)$$

adsorbent and  $\text{Co}(\text{Ad}\cdot\text{S})_x$  represents the adsorbent containing cobalt. When the quantity of adsorbent is increased, all other conditions remaining constant, the ratio of adsorbed to dissolved cobalt increased. A log-log plot of this ratio versus the concentration of adsorbent yielded a straight line of slope  $x$ . The value of  $x$  was found to be 1.2. They described this value as an "effective valence" indicating that the cobalt was present in solution partly as  $\text{Co}^{2+}$  and partly as  $\text{CoCl}^+$  or  $\text{Co}(\text{OH})^+$ . Both the exchange and hydrolysis

mechanisms were apparently operating. They also found that increased adsorption occurred with increasing pH, increasing quantities of adsorbent, and decreasing concentrations of ammonium chloride. However, no single expression was proposed to quantitatively relate these variables to the fraction of cobalt adsorbed. Application of these findings to soils and sediments is difficult since both of these natural systems are much more heterogeneous than the ideal system employed by Kurbatov. However, the existence of iron oxide clay skins in soils and sediments makes possible mechanistic speculations.

Mortensen<sup>68</sup> reviewed the role of soil organic matter in the complexation of metals. He concluded that soil organic matter forms complexes with metals by ion exchange, surface adsorption, and chelation mechanisms. Little is known concerning the ligands of soil organic matter which chelate metals, but carboxyl, alcoholic, phenolic, and amide groups are probably involved. Since quinone groups are known components of decomposing organic matter, Rashid<sup>69</sup> discussed their role in solubilizing and complexing metals in both sediments and soils. He was able to synthesize a copper benzoquinone complex. Additional evidence for the existence of trace metallo-organic complexes in soils was presented by Schnitzer<sup>70</sup> using differential thermal analysis and infrared techniques.

In general, studies of trace metal chelates with soil organic constituents have employed indirect methods to derive evidence for their existence. Considerably more work is needed using radiotracers and sophisticated separation and identification techniques in order to understand the chemistry of these complexes.

For example, a relatively new column chromatographic technique for isolating dissolved organic matter from sea water was used by Riley and Taylor.<sup>71</sup> They employed Amberlite XAD-1 adsorbents (Rohm and Haas) which are non-ionic, hard, insoluble

styrene polymers of large surface area. The components of dissolved organic matter are adsorbed in the order of their increasing hydrophobicity. Selective elution is accomplished by altering the hydrophobic nature of the adsorbed solutes. The authors were successful in recovering fatty acids, sterols, vitamins, surfactants, dyes, insecticides and humic acids. Similar adsorptive properties would be expected for soil organic matter extracts. The use of IR, GC, and MS techniques to analyze separated fractions should provide additional information on the composition of organic matter in soil and marine environments.

A very comprehensive discussion of possible mechanisms controlling concentrations of several trace metals in sea water was published by Krauskopf.<sup>72</sup> He suggested that the concentrations of Zn, Cu, Pb, Bi, Cd, Ni, Co, Hg, Ag, Cr, No, Sr, W, Ba, and V might be controlled by (a) precipitation of insoluble compounds with ions normally present in aerated sea water; (b) precipitation of sulfides in reducing environments; or (c) adsorption on ferrous sulfide, hydrated ferric oxide, hydrated manganese dioxide, apatite, clay, and organic matter.

Precipitation reactions were investigated by consideration of solubility product data and by experiments in which equilibrium concentrations of the metal ions were determined. Calculated and measured concentrations were in general agreement, but were uniformly larger than the observed concentrations in aerated sea water, except for barium and strontium. It appears that the concentrations of these metals are not controlled by solubility equilibria.

Although ocean circulation is effective in maintaining high levels of dissolved oxygen even at great depths, there are stagnant basins in isolated areas where the water

is depleted of its oxygen content due to high concentrations of decaying organic matter. Under these conditions, the chemical environment becomes reducing rather than oxidizing, which may lead to charge alteration and/or metal sulfide precipitation. Krauskopf investigated the solubilities of sulfides under generally accepted conditions for such stagnant basins; i.e., pH of 7 and hydrogen sulfide concentration of  $1 \times 10^{-3}$  M. Results indicated that, in local areas of very high sulfide concentration, precipitation of Cu, Zn, Cd, Bi, Hg, Pb, Ag, and Cr could produce the low concentrations found in sea water. However, these concentrations show no relation to their metal sulfide solubility. For example, the solubility product constants for CuS and ZnS differ by  $10^{21}$ , but the concentrations of dissolved copper and zinc are approximately equal in sea water.

The importance of adsorption in the control of metal ion concentrations is very difficult to determine quantitatively due to the variety of natural adsorbents present in sea water and the effects of temperature, pH, salinity, and amount and physical state of the adsorbent. Nevertheless, Krauskopf performed some semiquantitative experiments to compare the effectiveness of adsorption of several adsorbents in sea water for various metal ions. In all cases, the pH was adjusted to approximately 8, and the temperature ranged from 18 to 23°C. Concentrations of metal ions added were in the region of 0.1 to 10 mg/l; higher than natural concentrations but convenient for the spectrophotometric measurements employed. By his own admission, the results of these experiments may show marked divergence from the natural environment but they are meaningful in a comparative sense.

Briefly, the massive amount of data indicated that copper, zinc, and lead were adsorbed more strongly than the

other metals. All the adsorbents except plankton reduced the concentrations of copper, zinc, and lead within a few hours to nearly the normal concentration range found in sea water. Cobalt and nickel showed markedly less adsorption than copper, zinc, and lead despite the similarity of their ions in usual aqueous solutions. Of all of the adsorbents tested, manganese dioxide and iron oxide showed the greatest adsorptive capacities. However, there were several exceptions to these generalities, and Krauskopf concluded "the tables show little apparent correlation between the adsorptive behavior of the metals and their other chemical properties."

Krauskopf also considered the potential importance of trace metal concentration control by living organisms. This process could be of considerable importance since many organisms are known to exhibit large concentration factors relative to sea water. It is difficult to predict the time constant associated with this process, since decomposition of dead organisms should presumably release to the water substantial portions of these accumulated trace metals.

In summary, Krauskopf concluded that adsorption processes were probably the most important of those he considered in controlling trace metal concentrations in sea water.

A few other papers have appeared on the subject of trace metal adsorption in sea water. Goldberg<sup>22</sup> studied the ability of hydrated oxides of manganese and iron to selectively adsorb trace metals. It is an accepted fact that hydrous ferric oxide in sea water is electropositive and would therefore be expected to scavenge negatively charged ions. The hydrated oxides of manganese are electro-negative and, therefore, would be expected to concentrate

positively charged ions. However, after correlation analysis of trace metals adsorbed by these materials, Goldberg concluded that "both negative and positive sols will scavenge any given metal in solution with the majority of the element in question going to the sol carrying an opposite charge." However, Krauskopf found no support for the partitioning of positive and negative ions between these two sols.

Radioactive Co, Ag, Se, Cr, and Mo were used by Kharkar et al.<sup>73</sup> to study adsorption on various adsorbents in distilled water and subsequent desorption in sea water. In the adsorption work, concentrations of metals and sediment were chosen to simulate stream water conditions. They found that montmorillonite and illite, two common clay minerals, adsorbed approximately 90% of the cobalt, 20 to 30% of the silver, and 30 to 50% of the selenium. In contrast, freshly precipitated hydrous ferric oxide adsorbed 95% of the cobalt, 60% of the silver, and 90% of the selenium while reagent grade manganese dioxide adsorbed only 20% of the cobalt and 80 to 85% of the silver and selenium. Adsorption on kaolinite was generally much lower than on the other adsorbents. For chromium and molybdenum, there was no significant adsorption on any of the adsorbents.

When the montmorillonite and illite were transferred to sea water, approximately 40 to 70% of the adsorbed cobalt, 20 to 30% of the adsorbed silver, and 30 to 50% of the adsorbed selenium were released. Freshly precipitated ferric hydroxide released only negligible amounts of these three elements, but powdered manganese dioxide released almost the entire amount of silver and about 60% of the selenium but no cobalt. In general, trace elements adsorbed from distilled water are usually released, at least to some extent, on contact with sea water because of displacement by magnesium and



sodium ions which are present in very high concentration.

The most common clay mineral in marine sediments is illite. Chester<sup>74</sup> studied the adsorption of radioactive Zn and Co on illite in sea water at different temperatures. He reported that it required 60 hours for cobalt to reach equilibrium; whereas, zinc reached an equilibrium concentration in approximately 40 hours at 26°C. At this temperature, 48% of the cobalt and 92% of the zinc were adsorbed. As temperature increased, cobalt adsorption increased, but zinc adsorption decreased. Hodgson et al.<sup>75</sup> reported that the reactions of cobalt and zinc with illite are endothermic and exothermic respectively, which is in agreement with Chester's findings.

#### Analytical Characterization of Bottom Sediments

The chemical characteristics of marine sediments vary widely depending on whether they are from the deep sea or the near shore environment. Just as soils may be classified as acidic or alkaline, depending on the geological material from which they were derived and the environment in which they exist, so too marine sediments show similar variations. Hence, there are areas of calcareous oozes which are deposits containing more than 30% of organically-derived calcium carbonate. Likewise, there are siliceous oozes which are deposits containing more than 50% siliceous skeletal material. In other sediments, typical clays such as illite predominate, in which case the parent materials are largely minerals, rather than skeletal remains of living organisms.

The vast majority of marine sediment analyses have provided results on total concentrations of elements as a means of investigating genesis. In contrast, this study was focused on the surface characteristics of the fine material

(both inorganic and organic) because the interface between these surfaces and sea water can alter the concentrations of dissolved species.

Cation exchange capacity (CEC) and exchangeable cation status (ECS) are two very useful determinations in characterizing the surface status of sediments. CEC is a measure of the ability of the cations on the surface and within the crystal framework of the minerals and organic matter to be reversibly replaced by other cations which are either more strongly bound or present in higher concentration. It provides a relative numerical estimate of the capacity of a sediment to alter the concentration of dissolved species in sea water, especially when that sediment is suspended as would occur during offshore mining operations. ECS is a useful measure of the proportions of the several exchangeable metals present on the sediment. CEC and ECS are measured by saturating the sediment sample with a large excess of a selected cation usually followed by displacement with a second cation. ECS is determined by analyzing for specific metals in the leachate after initial saturation. CEC is determined by measuring the amount of initial saturating ion displaced by a second saturating ion.<sup>76</sup>

In addition to measuring the concentrations of exchangeable cations using a neutral salt solution, it is informative to employ acid extractions to estimate the amounts of readily soluble species present. In some cases, measurement of total concentrations to permit classification of the sediment is helpful in understanding its surface properties. X-ray diffraction techniques can also be used to identify principal mineralogical species.

Another important characteristic of sediments is the organic content and its degree of decomposition. In addition

to being the major source of sulfur, nitrogen, phosphorus, and other nutrients, well-aged organic matter has a very high CEC; typically 150 to 200 meq/100 g in contrast to values of 20 to 40 meq/100 g for common clay minerals such as illite. The amount of organic matter can be estimated by measuring the chemical oxygen demand (COD)<sup>77</sup> or by combustion techniques. The latter procedure allows measurement of the nitrogen content, which is useful in classifying the degree of decomposition, but gives no distinction between organic and inorganic carbon unless samples are pretreated.

## DESIGN OF THE EXPERIMENT

In the exploratory stages of the field dredging study, a large number of cores were obtained from the dredge site using an Alpine Vibracorer (Alpine Geophysical Associates, Inc.). These cores ranged in depth from 3 feet to 18 feet. They were cut into 30-inch lengths, capped, and frozen in dry ice on-board ship. Each day the cores were transported to the University and stored frozen until analyses could be performed.

In order to conduct equilibration studies with trace metals, a bulk sample of -230 mesh material was required. The core samples taken from the dredge site where sand and gravel content was very high generally contained only 1-3% -230 mesh particles. Consequently, it would have required an extremely large number of cores to accumulate sufficient sample for equilibration experiments. To circumvent this problem, a site adjacent to the dredge area containing a substantially higher percentage of -230 mesh particles was sampled. The location is shown in Figure 1. The similarity of the -230 mesh material from this site to the -230 mesh material from several dredge area sites was established experimentally before the material was used in equilibration work.

Selection of the independent variables to be manipulated during equilibration studies was based on actual differences expected to occur in the field trials. Prior investigations had shown that the typical temperature at a depth of 100 feet was 4°C, whereas, the expected water temperature at the surface where the dredge spoils would be discharged during the test period was expected to be approximately 18°C. Light levels are quite high for the first 10 to 15 feet below the

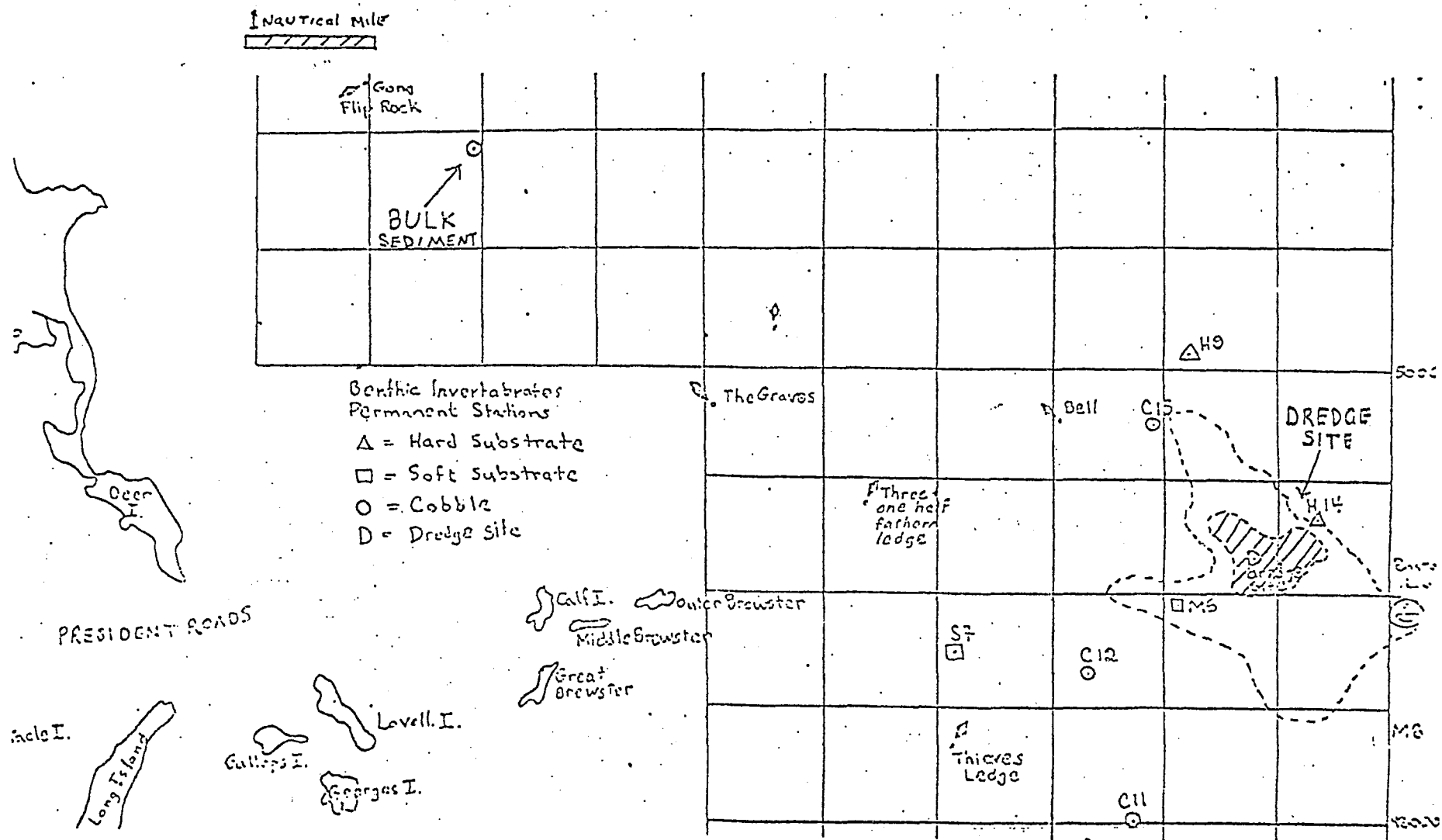


Fig. 1 Location of Dredge Area

surface but very low at the 100-foot depth. This could induce photochemical changes. A third variable was oxygen content since there was evidence that the oxygen content at the sediment-water interface would be significantly lower than at the water surface. pH was not included as a variable since there was no data to suggest pH differences between the surface and the deep water. However, pH inadvertently became a major variable in the study due to the method used to control oxygen concentrations.

It is common to conduct equilibration experiments over a period of several days. However, for the combinations of independent variables employed in this experiment, precise control of these variables for such a period of time would have been very difficult. Consequently, preliminary studies were conducted at room temperature, ambient light levels, and normal dissolved oxygen concentrations to estimate the time required for the metals Pb, Cu, Zn, Cd, Co, and Ni to reach equilibrium in sea water-sediment suspensions. The sea water was "spiked" with 100 ug/l of each metal. These studies were conducted over a period of seven hours with aliquots being withdrawn on the hour. After filtering, the dissolved metal content of the filtrates were determined by solvent extraction-atomic absorption spectrophotometry. From the preliminary experiments, it was decided that sampling should be conducted at 3, 7, 13, 20, 30, 50, 70, 90, 120, and 180 minutes. The choice of three minutes as the shortest sampling time was necessitated by the time required to remove a 500 ml aliquot and filter it on a Büchner funnel. The choice of a 180-minute final sampling was based on the difficulty in maintaining independent variables constant over longer periods of time coupled with the close approach to equilibrium during this time.

A  $2^3$  factorial experiment was used to investigate the

effects of oxygen, temperature, and light levels on the rate of adsorption of trace metals from "spiked" sea water as well as the extent of adsorption after three hours. As mentioned earlier, the manipulation of oxygen content was later found to induce a pH change; consequently, these two variables were confounded. Another factorial experiment was conducted to separate their effects.

The data obtained from the  $2^3$  factorial experiment were analyzed by multiple regression analysis techniques. In this approach, the total variance of the response variable (metal remaining in solution) was fractionated into the portions caused by each of the independent variables individually and in combination.

In separate studies, the cupric specific ion electrode was employed to obtain data on the speciation of this metal under various conditions. It was also employed as a means of estimating the total copper concentration in sea water by comparing results derived with this method to those from the solvent extraction-atomic absorption spectrophotometric procedure.

## EXPERIMENTAL

The frozen core samples, contained in three-inch diameter polyvinyl chloride tubes, were thawed, extruded, and promptly prepared for analysis. The bulk sample, contained in 3.5 gallon acid-washed polypropylene buckets, was not frozen but it was delivered to the laboratory for preparation within a few hours of sampling. The preparation scheme is summarized in Figure 2.

The -230 mesh material was isolated by wet screening successively through 10 mesh and 230 mesh stainless steel screens using sea water. The 10 mesh screen removed shells, rocks, and small pebbles, thereby reducing the loading on the 230 mesh screen. Sea water was used rather than distilled water to minimize chemical alteration of the sediment surface. After passing the 230 mesh screen, suspensions were filtered on acid-washed, porcelain Büchner funnels fitted with Whatman No. 40 paper.

The -230 mesh material from the core samples generally represented a relatively small amount of material which was placed in small polyethylene bags. For the bulk sample, the filter cakes, totalling approximately 30 pounds, were homogenized in a polypropylene bucket. Samples were taken from the top, bottom, middle, and sides of the bulk sample for moisture determinations as a means of estimating the degree of homogeneity achieved. The average moisture content was 31.64%, and the relative standard deviation was 0.43% which was taken as adequate evidence of the homogeneity of the sample. All samples were stored moist at 4°C. Separate moisture determinations corrected sample weights to a dry



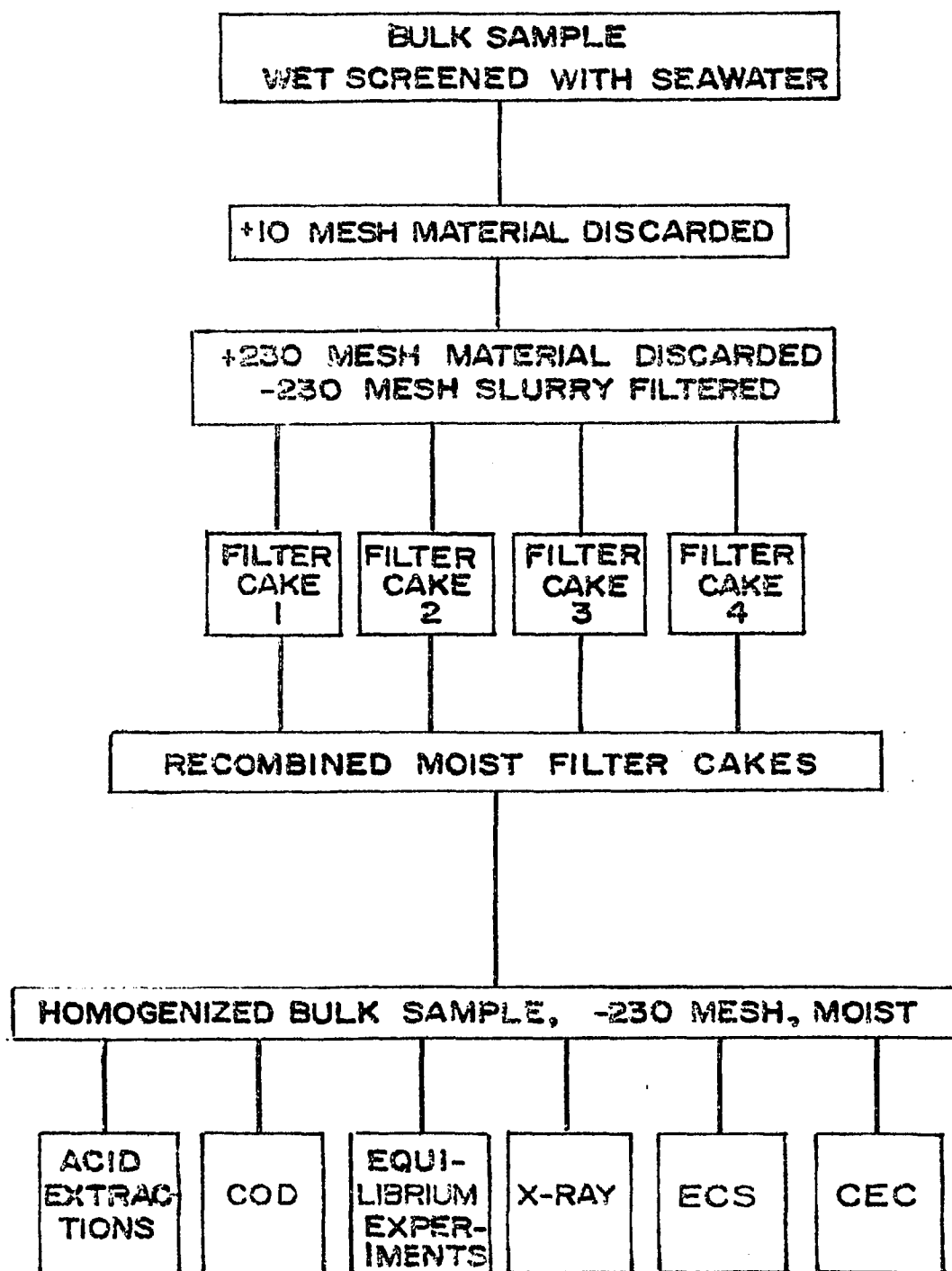


Fig. 2 Sample Preparation Scheme

weight basis. Toth and Ott<sup>78</sup> and others have shown that drying of samples prior to analysis exerts considerable effects on several determinations, especially CEC and ECS.

Core samples and the bulk sample were analyzed to generate baseline data which could be used in the interpretation of field and laboratory experiments respectively. Analyses performed were (a) hydrochloric acid extractable metal concentrations; (b) total metal concentrations for the bulk sample; (c) CEC; (d) ECS; (e) organic carbon content; and (f) mineralogical characterization.

Extractable metal concentrations were estimated using both 0.1 and 0.5M HCl prepared from 6M HCl, which was distilled from an all-Pyrex apparatus. Acid prepared in this manner has been found to contain acceptably low concentrations of the metals of interest. The use of 0.1M HCl provided information on metals which were in a fairly readily soluble form, whereas the 0.5M HCl treatment extracted those metals which were more strongly bound to the sediment. In addition, some of the core samples contained large amounts of aragonite (a form of calcium carbonate) which consumed most of the 0.1M HCl, thereby making extractions with 0.5M HCl desirable.

In these extractions 50 ml of acid were added to moist sediment samples of approximately 9 grams contained in acid-washed, Pyrex beakers. After heating for approximately 30 minutes, the suspensions were filtered through acid-washed Whatman No. 42 paper and the filtrates made to 100 ml with high purity water. Metals were determined after appropriate buffering by atomic absorption spectrophotometry (AAS). All standards were synthesized to simulate the matrix of the sample solutions.

A pressure decomposition technique (79, 80) was used to generate information on the total metal concentration of

the bulk sediment. Approximately 0.1 g samples were treated in Teflon-lined bombs using aqua regia and HF. Samples were quantitatively transferred to 125 ml acid-washed, polypropylene beakers containing 5.6 g of boric acid in solution to form soluble metal fluoroborates. This solution was transferred and made to volume in acid-washed, 100 ml polypropylene volumetric flasks. Metals were determined by AAS after appropriate buffering and with standards containing the same matrix as the samples. The determination of total mercury was performed by flameless AAS on four cores and the bulk sediment according to the procedures of Hatch and Ott<sup>81</sup> and Cranston and Buckley.<sup>82</sup>

All atomic absorption measurements were made with a Techtron AA3 modified with AA5 electronics and a DI-30 digital display unit. Hollow cathode lamps by Atomic Spectral Lamps, Perkin-Elmer, and Westinghouse were used. Both R106 and R136 photomultiplier tubes, supplied by Techtron, were used depending on the element being determined. Polyvinyl capillary tubing was used to introduce the aqueous solutions to the nebulizer, but with MIBK, it was necessary to employ polytetrafluoroethylene capillary tubing.

CEC measurements were performed by saturating known weights of sediment contained in polyethylene centrifuge tubes with 1M calcium chloride solutions. Excess calcium chloride was removed by washing with 70% methanol, followed by centrifuging (Sorval Model RC-2B) until the solution was chloride-free. The calcium was displaced using 1M ammonium acetate. After centrifugation, the calcium in solution was determined by AAS.<sup>76</sup> Some of the core sediments were later found to contain large amounts of aragonite which is quite soluble in ammonium acetate, causing high values for the CEC.

To determine the ECS, sediment samples were first washed with 70% methanol to remove interstitial sea water. The exchangeable cations were displaced using a 1M ammonium acetate solution. The suspension was filtered through previously washed Whatman No. 42 paper and the filtrate analyzed by AAS.<sup>76</sup> Only the major cations were determined by this procedure.

Organic carbon content was estimated in two ways. COD was determined using the dichromate oxidation procedure.<sup>77</sup> Ballinger and McKee<sup>83</sup> provided an empirical conversion factor to relate the approximate percent organic carbon to the COD value. In addition, the total CH&N was determined by combustion (F & M Scientific Corp., Model 185). This analysis was performed on untreated and HCl-treated samples of the bulk sediment. The HCl-treated sample was free of carbonate carbon.

Mineralogical composition was obtained from X-ray diffraction analyses performed on a Phillips-Norelco X-ray diffractometer using copper  $K_{\alpha}$  radiation

The solvent extraction-AAS determination of trace metals was adapted from the APCD-MIBK procedure proposed by Brooks et al..<sup>35</sup> Using 500 ml of sea water, treated with APCD and 25 ml of MIBK, it was possible to determine Pb, Cu, Zn, Cd, Ni, and Co concentrations in both natural and "spiked" samples. It was necessary to determine the solubility of MIBK in sea water of varying salinity at 25°C in order to apply corrections for samples of varying salt content.

To accomplish the extraction, 500 ml samples were placed in one liter polypropylene flasks (Nalge-Sybron Corporation). Phosphate buffer, purified by three extractions with APCD-MIBK, was added to adjust the pH approximately to 6. APCD (Kodak No. 9279) was added as a 1% aqueous solution followed by 25 ml of MIBK (Kodak No. 13033). Both of these reagents

were used as received. Flasks were agitated for 30 minutes on a wrist action shaker (Burrell Corporation) and then transferred to separatory funnels fitted with Teflon stopcocks. The MIBK extracts containing the metal-APCD chelates were stored in acid-washed, polyethylene bottles in anticipation of AAS analysis.

Standards were prepared by adding 10 ml of MIBK to each sample of sea water previously extracted. After a 5-minute equilibration, the phases were separated and the several portions of MIBK-saturated sea water combined to insure homogeneity. From this large sample, 500 ml portions were placed in individual polypropylene flasks. Incremental amounts of the six metals to be determined were added to the various flasks covering the range 0 to 100 ug/l. Following the APCD and buffer additions, the appropriate amount of MIBK was added (approximately 15 ml) based on the solubility of MIBK in the sea water. After the usual 30-minute shaking procedure, the phases were separated as described previously; and both standards and samples were analyzed using AAS with an air-acetylene flame.

Equilibrium experiments were performed in a carefully cleaned, four-gallon, polypropylene bucket containing 10 liters of unfiltered sea water from Rye, New Hampshire. One hundred and fifty grams of bulk wet sediment (approximately 100 g dry weight) were added to the bucket. This was followed by 10 ml of 100 mg/l solution containing Pb, Cu, Zn, Cd, Ni, and Co to give a final concentration in solution of 100 ug/l.

Nine experiments were conducted corresponding to the appropriate combinations for a  $2^3$  factorial with temperature, oxygen level, and light as the three variables. The ninth run was a control in which no sediment was present. Temperature was maintained at either 4°C or 20°C by immersing the test

container in a water bath in which the temperature was controlled using water and ice. Oxygen content was manipulated by continuously bubbling either air or nitrogen into the mixture through gas dispersing frits. A polyethylene stirrer provided homogeneity of the sediment-water mixture. Dissolved oxygen content was monitored with a Model 54 dissolved oxygen meter and BOD probe (Yellow Springs Instrument Company). Saturated values were approximately 10 mg/l at 4°C and 7 mg/l at 20°C. When nitrogen was being bubbled into the system, the oxygen content was approximately 1.5 mg/l for both temperatures. Light conditions of approximately 4000 Lux (the level used for phytoplankton growth) were maintained with a Model F40D "Daylight" 40-watt fluorescent tube (Sylvania Corporation). Dark conditions were produced by covering the bucket with black paper. Light levels in the suspension were measured with a Model 65 Radiometer light meter (Yellow Springs Instrument Company).

At ten predetermined times over a three-hour period, 500 ml aliquots of suspension were siphoned with Tygon tubing into an acid-cleaned, graduate cylinder. Suspensions were immediately filtered through acid-washed Whatman No. 40 paper in Büchner funnels and transferred to polypropylene flasks for extraction. Acid washing of the filter paper was essential to reduce zinc blanks to an acceptable value. Each filtrate was analyzed for the six metals of interest by the solvent extraction-AAS procedure.

All studies of cupric ion content by specific ion electrode techniques were made using a Model 407 specific ion meter and a Model 94-29A cupric ion indicator electrode with a Model 90-01 single junction silver/silver chloride reference electrode (Orion Research, Inc.).

## RESULTS AND DISCUSSION

### Characterization of Sea Water

For broad scale application of the solvent extraction-AAS technique, it was necessary to determine the variation in solubility of MIBK as a function of salinity and also to demonstrate quantitative recovery of the six metals of interest in this study. Although it was not anticipated that salinity would vary over an extremely wide range, a study was conducted to determine the percent solubility of MIBK on a v/v basis in sea water ranging in salinity from 0 to 30‰. This was accomplished by adding a known volume of MIBK to sea water of varying salinity contained in a separatory funnel at 25°C. After shaking, the MIBK was placed in a tared polypropylene bottle and weighed. Using the density of MIBK, the solubility was calculated. The relationship is illustrated in Figure 3 and was used as the basis for minor corrections.

It was essential to minimize the amount of sample handling and reagent usage to avoid contamination. Ideally, the buffer, APCD, and MIBK would be added directly to the sea water without any treatment to destroy organic matter or otherwise alter the matrix. This requires that the stability constants of the metal-APCD complexes be greater than the stability constants of other complexes which the metals might form. To test this, a bulk sample of sea water from Rye, New Hampshire, was doped with five levels of each of the six metals covering the range 5 to 100 ug/l for each metal. This concentration range was selected because it was to be used in equilibration studies. The amounts of metal added are unlikely

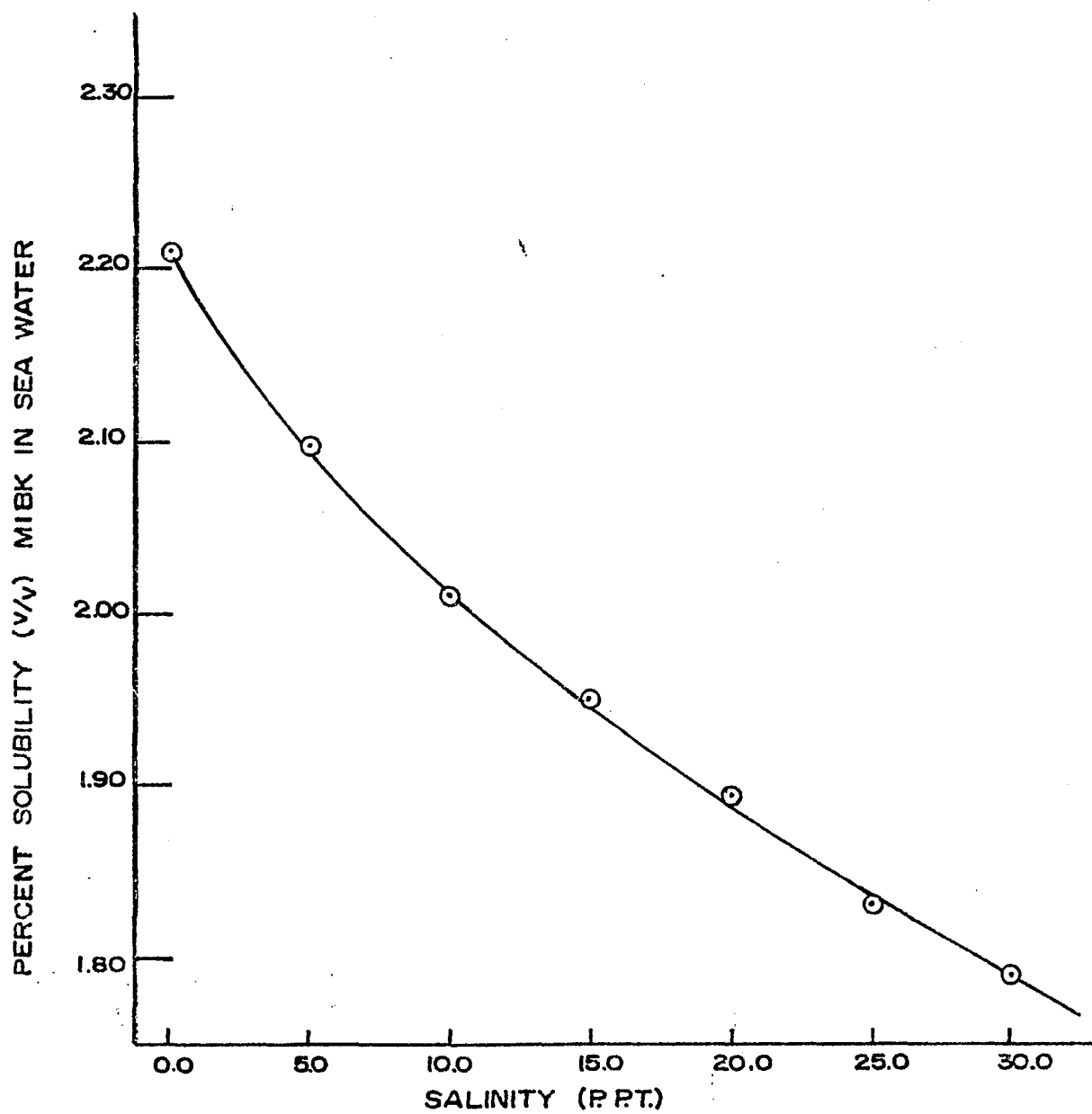


Fig. 3 Per Cent Solubility of MIBK in Sea Water of Varying Salinity



to induce major changes in the equilibria between the metals and their various complexes. The data summarized in Table 3 provided adequate justification for omitting chemical pre-treatment of the sea water. The averages of triplicate recoveries varied from 97% to 100% and showed no tendency for low recoveries at the small spiked concentrations. The highest level for cadmium is not reported because the calibration curve for this element deviated substantially from Beer's law above concentrations of 50 ug/l.

A bulk sample of sea water collected from Rye, New Hampshire, was analyzed by AAS for the four major cations, Na, Mg, Ca, and K, and the six trace metals considered in this study. Volumetric chloride analyses provided a salinity estimate of 32.52 ‰. In Table 4, average concentrations for the four major cations are compared with predicted values for this sample.<sup>84</sup> Agreement between experimentally measured and expected values is quite good for each of the four elements. The average values reported for the trace metals are within the generally accepted ranges for sea water. The variability of replicate measurements was quite large because the concentrations were near the detection capability for the procedure used. For example, in the case of copper, values varied from a low of 1.0 to a high of 3.0 ug/l for the 14 determinations which were made over a time span of about one year. Better precision could have been obtained by using larger samples of sea water, but it was impossible to rapidly filter more than 500 ml for the equilibration work, and it seemed best to maintain constant conditions for all measurements.

Before attempting measurements of copper speciation, experience was gained with the copper specific ion electrode by making measurements of total copper concentrations for

TABLE 3

## RECOVERY OF TRACE METALS FROM "SPIKED" SEA WATER

<u>Concentration Added, ug/l</u>	<u>% Recovery of Individual Metals*</u>					
	<u>Cu</u>	<u>Pb</u>	<u>Co</u>	<u>Ni</u>	<u>Cd</u>	<u>Zn</u>
5.0	96	100	98	96	105	100
10.0	97	100	98	99	105	98
20.0	94	100	100	94	100	100
40.0	96	93	97	96	94	94
100.	100	95	100	100	**	95
Average % Recovery	97	98	99	97	101	97

\*Each value is based on three independent analyses involving the total analytical process.

\*\*Values above 50 ug/l not determined due to deviations from Beer's law.

TABLE 4

## METAL COMPOSITION OF SEA WATER FROM RYE, NEW HAMPSHIRE

	Major Cations, mg/l	
	<u>Measured, AAS*</u>	<u>Predicted**</u>
Na	10,100	9,990
Mg	1,180	1,201
Ca	403	383
K	377	359

	<u>Minor Cations, ug/l by Solvent Extraction-AAS***</u>
Cu	1.9
Pb	2.4
Zn	2.1
Ni	1.8
Co	1.
Cd	1.

\*Based on duplicate determinations.

\*\*Based on salinity of 32.52‰.<sup>84</sup>

\*\*\*Based on 9 determinations except copper which was based on 14.

comparison with the solvent extraction-AAS results. A number of difficulties were encountered. Electrode response was observed to be light sensitive, and stirring rate had a pronounced effect. Shielding the electrode from room light with black paper was considered, but this method was discarded since it interfered with visual access to the container. It was found adequate to carefully reproduce the ambient light conditions and stirring rate so that they did not vary significantly between measurements. In a paper published after this work was completed, Smith and Manahan<sup>85</sup> used a unique jacketed glass cell filled with methylene blue and a special spiral-shaped glass stirrer to overcome these problems.

Another difficulty was the very long response time of the electrode when employed at the  $\mu\text{g/l}$  concentration level. For example, 30 to 60 minutes were often required to achieve a stable potential reading. In some cases, Time Response Paper was used to obtain the potential at infinite time by extrapolation. The usefulness of this approach was demonstrated by making a series of aqueous copper standards ranging in concentration from 1 to 100  $\mu\text{g/l}$ . The millivolt readings obtained at different times and the graphical values for  $t_{\infty}$  are shown in Table 5. The  $t_{\infty}$  values were used to construct a calibration curve (Figure 4). While the points exhibited some scatter and the slope was somewhat less than the theoretical value of 29.6 mV/decade, results provided encouragement that the very low concentrations in sea water could be measured.

The known addition procedure was employed using both the known increment scale on the specific ion meter and the Gran's Plot technique. Reproducibility with the known increment scale procedure was achieved with difficulty because the initial measurement and the measurement after a single addition were both made in extremely dilute solutions. Time Response

TABLE 5

## ELECTRODE RESPONSE IN DILUTE AQUEOUS SOLUTIONS

Cu <sup>2+</sup> in Water ug/l	Potential (mV)				t <sub>∞</sub> Extrapolated
	Minutes				
	10	15	20	25	
1	-95.0	-87.0	-84.0	-82.0	-76.0
10	-62.5	-54.5	-52.0	-51.5	-46.0
50	-50.0	-42.0	-39.0	-37.5	-31.7
100	-31.3	-27.0	-25.5	-24.5	-21.0

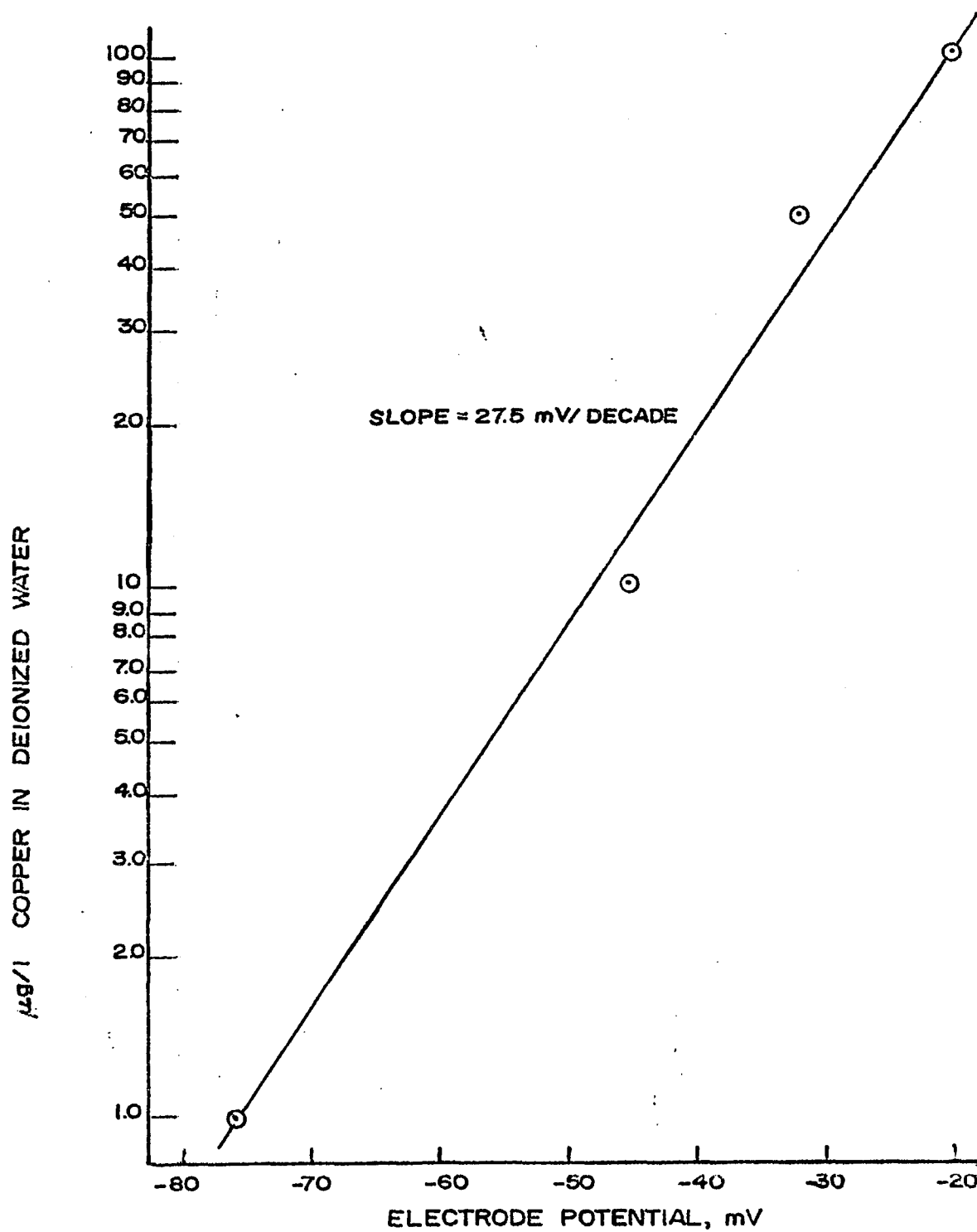


Fig. 4 Copper Calibration Curve in Dilute Aqueous Solutions

Paper cannot be used because a ratio is recorded instead of potentials. Thus long waiting times were required to achieve stable readings. Using the Gran's Plot approach in which potentials can be recorded, several additions were made. As concentration increased, the ease of achieving precise electrode readings improved. Further, the benefit of drawing a line through several points was realized. Consequently, a single erratic point in the very low concentration range exerted less influence on the final result. Comparison of measurements made by these three techniques is presented in Table 6. While there is some variation in the means from the three procedures, an analysis of variance indicated that the differences were not significant at the 95% probability level. Agreement between the values from the Gran's Plots and the solvent extraction-AAS procedure was quite good for this concentration range. Surprisingly, the standard deviation for the known increment scale measurements was slightly smaller than for the other techniques, but the difference was not statistically significant.

In order to estimate ionic copper concentration, calibration of the specific ion electrode in a medium of ionic strength similar to sea water was required. Following the suggestion of Stiff<sup>51</sup>, 0.70 M KNO<sub>3</sub> was used since it is a noncomplexing salt. Copper concentrations ranging from 10,000 to 100 ug/l were prepared in this solution. Lower concentration standards were not synthesized due to the contamination potential from the large amount of potassium nitrate present. An excellent Nernstian response curve was obtained for these standards, but it was necessary to use the absolute millivolt scale with a range of -1000 to +1000 millivolts in order to extrapolate the curve to the concentration region found in natural sea water. In comparison to

TABLE 6

COMPARISON OF ATOMIC ABSORPTION AND  
SPECIFIC ION ELECTRODE TECHNIQUES FOR THE  
DETERMINATION OF TOTAL COPPER IN SEA WATER

<u>Concentration of Copper, ug/l</u>		
<u>Solvent Extraction-AAS</u>	<u>Gran's Method</u>	<u>Known Increment Scale</u>
3.0	2.3	2.5
2.0	3.0	3.5
1.0	2.0	3.3
1.8	1.5	2.7
1.0		1.8
1.1		2.6
3.0		
2.0		
1.1		
2.0		
2.4		
1.6		
2.5		
2.5		
Range: 1.0-3.0	1.5-3.0	1.8-3.5
Ave: 1.90	2.20	2.70
S <sub>y</sub> : 0.70	0.63	0.61

From ANOVA, it was concluded that there was no difference between the means at the 95% probability level.

$$F_{\text{calc}} = 3.0 \quad F_{\text{table}} = 3.47$$



the expanded scale of -100 to +100 millivolts used in the Gran's Plots, precise reading of the scale was difficult. The average free ionic copper concentration based on independent duplicate measurements was 0.001 ug/l. This extremely low value, corresponding to approximately 0.05% of the total copper, implied that organic ligands might be playing an important role. Zirino and Yamamoto<sup>23</sup> estimated that there should be about 1% ionic copper at pH8.1 based on inorganic complexes only.

An attempt to determine the importance of organic ligands was made by nitric acid digestion of a sample. To reduce possible copper contamination by the nitric acid, the sea water was made 10% in nitric acid and refluxed for 1 hour. Preliminary measurements on these solutions gave abnormally high values for ionic copper leading to the suspicion that the electrode might not be functioning properly. To test this possibility, copper standards ranging from 1 to 25 mg/l in 0.70 M potassium nitrate were prepared. Repeated measurements in these standards gave slopes ranging from 14 to 20 mV/decade. The electrode surface was cleaned using ammonia even though chloride poisoning was not suspected. The next trial produced a Nernstian response (Figure 5). Further measurements in the nitric acid digested solutions again produced incorrect results. This time the crystal membrane was gently polished on very fine alumina in order to produce a new membrane surface. Nernstian response returned for the 1-25 mg/l standards after this treatment (Figure 5). At about this time, the paper by Smith and Manahan<sup>85</sup> appeared in which they stated that, in an oxidizing medium, the cupric ion electrode yields potentials which are incorrectly high. They postulated that this interference was caused by the oxidation of sulfide on the crystal surface. Although it had been planned to neutralize the excess nitric

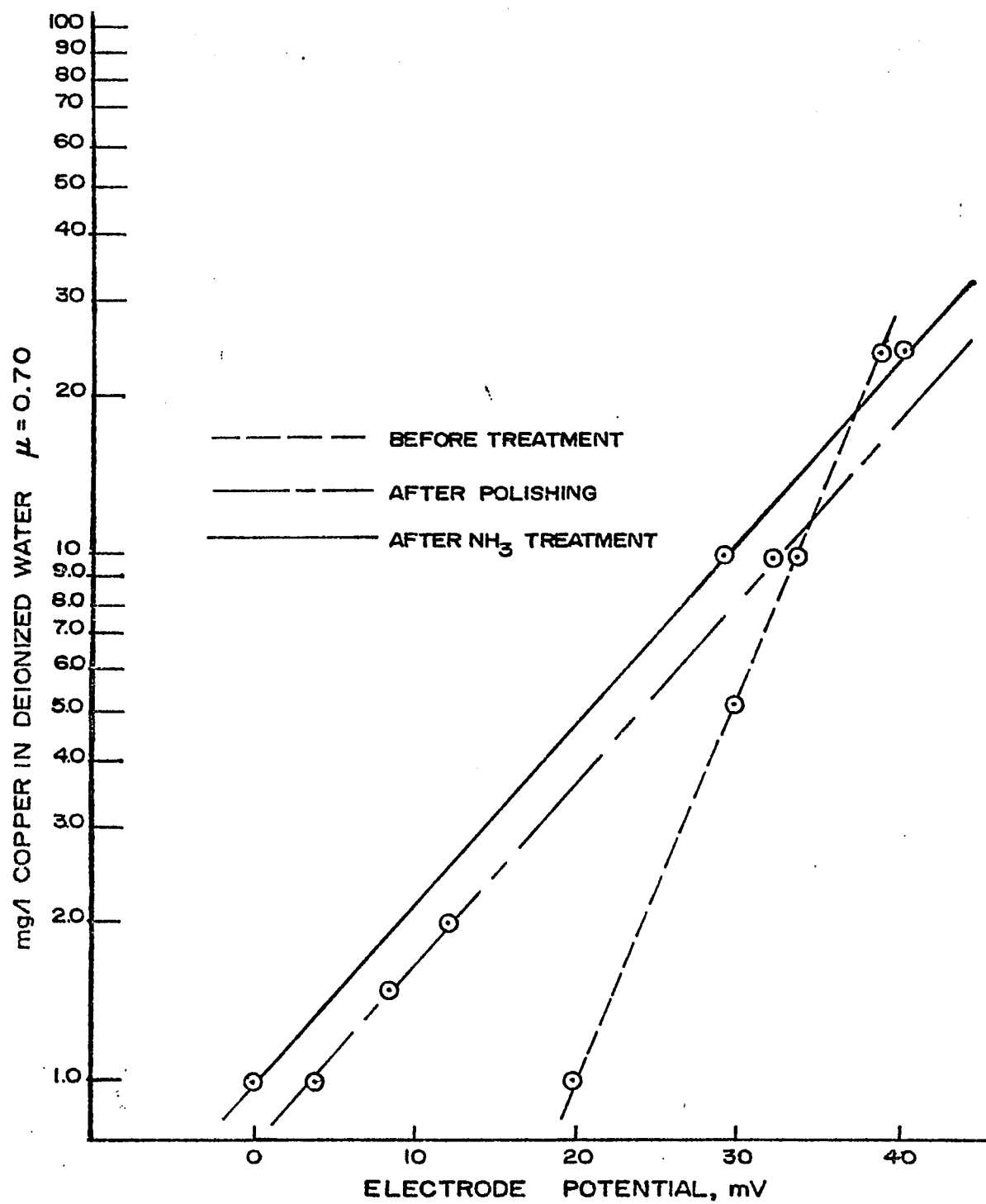


Fig. 5 Electrode Response Before and After Polishing and NH<sub>3</sub> Treatments

acid with purified alkali, successful measurements on solvent extracted sea water led to the abandonment of the wet oxidation approach.

Organic matter extraction was attempted by using two successive extractions with hexane at the natural pH of sea water. Copper in the amount of 200 ug/l was added to aliquots of extracted and non-extracted sea water. Specific ion electrode measurements on these samples indicated no measurable difference in the concentrations of free ionic copper. Either hexane was not a satisfactory extractant for the organic matter involved in copper complexation, at least under the conditions employed in this test, or organic matter was not an important factor in copper complexation.

Typical organic matter in sea water contains many weak acids which are not dissociated at pH 2 and can be extracted at that pH by chloroform.<sup>29</sup> This approach was employed, and after extraction, the pH was raised to its normal value of 8.1. Duplicate aliquots of extracted and non-extracted sea water were spiked with copper to levels of 100, 200, 300, 400, and 500 ug/l. Although the concentrations of ionic copper were still extremely low relative to the amounts of copper added, consistent differences between the normal sea water and the chloroform extracted sea water were observed (Table 7). For additions up to 500 ug/l, the chloroform extracted sea water always showed approximately three times as much ionic copper as in the normal sea water. Still, the concentration of ionic copper in the extracted sea water was only 0.1%, lower by a factor of 10 than the predicted values in the absence of organic matter.<sup>23</sup> Of course, it is certain that all organic ligands such as weak bases were not extracted by the chloroform so a significant concentration of organically bound copper may have remained. It is also possible that some copper,

TABLE 7

PERCENT IONIC COPPER IN  
UNTREATED AND CHLOROFORM EXTRACTED (pH 2) SEA WATER

<u>ug/l Added Copper</u>	<u>Concentration Cu<sup>2+</sup> (ug/l)</u>		<u>Percent Ionic Copper*</u>	
	<u>Untreated</u>	<u>Chloroform Extracted**</u>	<u>Untreated</u>	<u>Chloroform Extracted</u>
0	0.001	--	0.05***	--
100	0.030	0.09	0.03	0.09
200	0.066	0.20	0.03	0.1
300	0.095	0.29	0.03	0.1
400	0.14	0.40	0.04	0.1
500	0.18	0.50	0.04	0.1

\*Based on the amount of copper added.

\*\*Sea water extracted at pH 2 with CHCl<sub>3</sub>. The pH then readjusted to 8.1.

\*\*\*Based on a total copper concentration of 2.2 ug/l.

originally complexed by organic ligands, was converted to the hydroxide complex when the pH was raised to 8.1.

According to the model of Zirino and Yamamoto<sup>23</sup>, there should be a marked pH dependence of ionic copper concentration between pH 7 and 9. At pH 7 they predicted that 30% of the copper is present as  $\text{CuCO}_3^\circ$ , 20% as  $\text{Cu(OH)}_2^\circ$  and 30% as  $\text{Cu}^{2+}$ , with the remainder split among several species. At pH 8.1, 90% is present as  $\text{Cu(OH)}_2^\circ$ , 8% as  $\text{CuCO}_3^\circ$ , and  $\text{Cu}^{2+}$  and  $\text{Cu(OH)}^+$  each represent about 1% of the total.

The relationship between pH and ionic copper concentration was measured by spiking a normal sea water sample with 200 ug/l of copper. This concentration level was chosen to be adequate for reasonable electrode response times. After acidifying the sample with distilled hydrochloric acid to pH 7, electrode measurements were made while the pH was systematically raised to pH 9 using sodium hydroxide. The results are plotted in Figure 6. At pH 7, the percent  $\text{Cu}^{2+}$  is approximately 0.28% while at pH 8.1, it is only 0.06%, in reasonable agreement with the results obtained earlier (Table 7). At pH 9, the percent copper as  $\text{Cu}^{2+}$  is 0.02%. The large relative decrease between pH 7 and 8 and a more gradual decrease with further pH increase is in accord with Zirino and Yamamoto. The pH dependence for sea water extracted with chloroform as described earlier was found to be the same as the untreated water, except that the curve was displaced to higher percentages of ionic copper.

In addition to providing experimental estimates of the extent of copper complexation in sea water, it was hoped that the electrode could be used for continuous in situ monitoring of copper concentrations during the equilibration studies. However, based on accumulated evidence, it was apparent that this would be impractical. It was possible to determine both total and ionic copper in sea water with the specific ion

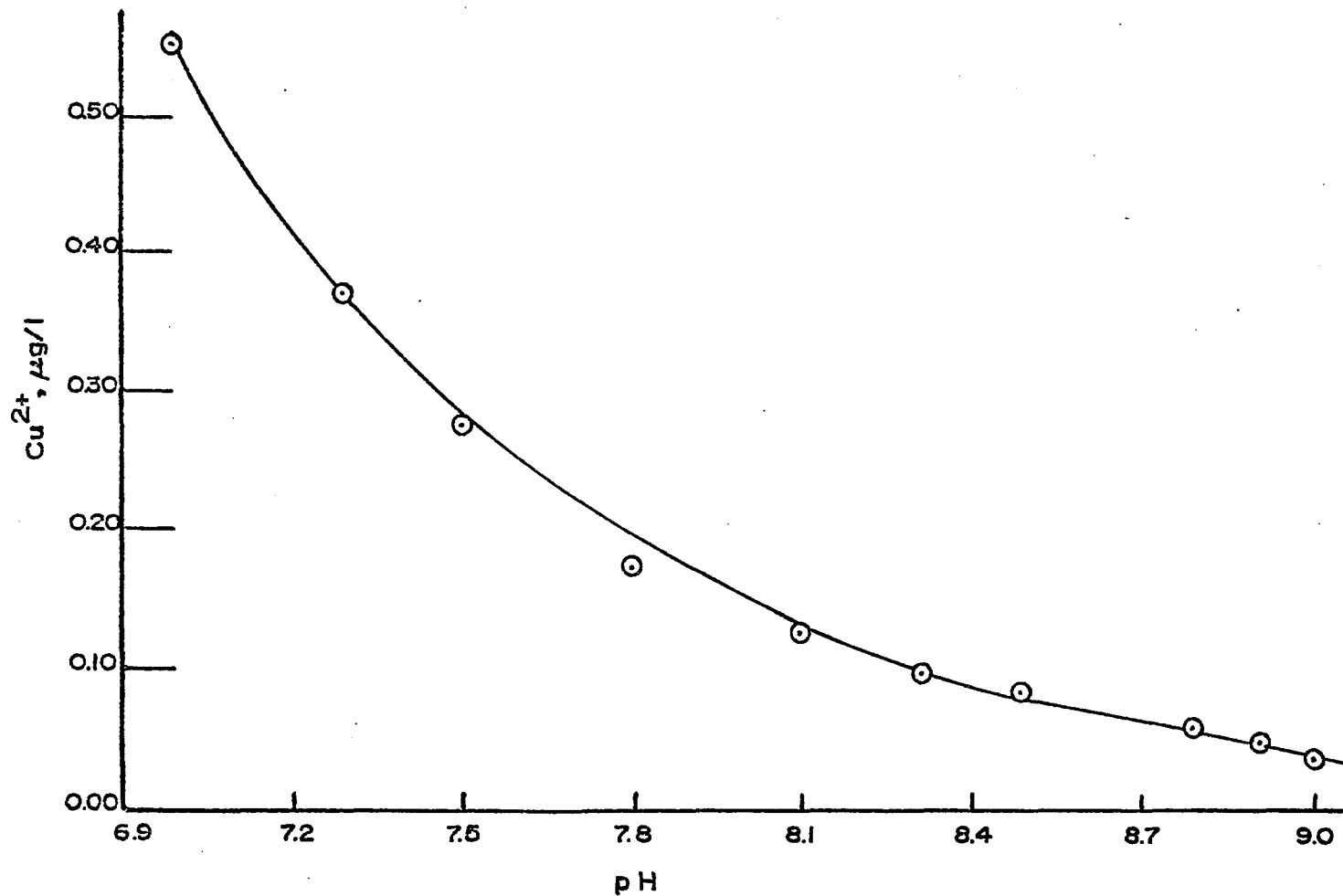


Fig. 6 Ionic Concentrations as a Function of pH for Sea Water Spiked with 200  $\mu\text{g/l}$  Copper

electrode. However, total copper concentration could not be inferred from continuous measurement of ionic copper because (a) the fraction of total copper in the  $\text{Cu}^{2+}$  state was so small that minor changes in this fraction would have a drastic effect on the predicted total copper concentration; (b) electrode response time was too slow at this concentration level of  $\text{Cu}^{2+}$ ; (c) small deviations of pH from the normal value of 8.1 caused large variations in the proportion of  $\text{Cu}^{2+}$ ; and (d) changes in the concentration of dissolved organic matter also altered the proportions of  $\text{Cu}^{2+}$ . Consequently, the solvent extraction-AAS procedure, which was found to provide reliable quantitative results, was employed. This limited data acquisition to several specific times during the equilibration period.

#### Characterization of Bulk Sediment

Total concentration data on the -230 mesh bulk sediment for the major and several trace metals were obtained from duplicate measurements by the bomb dissolution technique (Table 8). All of these concentrations were estimated by AAS analysis of the fluoroborate solutions except for mercury which was determined by the "cold vapor" method.<sup>81,82</sup>

Comparisons of the concentrations of trace metals in the -230 mesh fraction of this bulk sample with abundances in the lithosphere, illite, and other marine sediments indicated higher than normal concentrations of chromium, lead, and cadmium (Table 9), possibly due to man-induced contamination. In the cases of chromium and cadmium, biological scavenging could conceivably be involved since these two elements show very large concentration factors in shellfish.<sup>86</sup> Mercury, which has received considerable attention of late, was present

TABLE 8

## TOTAL AND ACID EXTRACTABLE CONCENTRATIONS IN THE -230 MESH BULK SEDIMENT

Major Elements %	Total Concentration	Concentration Soluble in 0.1M HCl	% of Total Soluble in 0.1M HCl	Concentration Soluble in 0.5M HCl	% of Total Soluble in 0.5M HCl
Na	1.8	0.10	5.6	0.16	8.9
K	1.5	0.070	4.7	0.23	15.
Ca	0.31	0.28	90.	0.33	106.
Mg	2.6	0.13	5.0	0.36	14.
Fe	6.2	0.44	7.1	1.2	19.
Minor Elements ug/g					
Zn	100.	63.	63.	76.	76.
Cr	310.	52.	17.	130.	42.
Cd	11.	1.0	9.1	1.2	11.
Ni	63.	7.7	12.	14.	22.
Cu	58.	22.	38.	43.	74.
Co	57.	3.0	5.3	6.0	11.
Mn	550.	64.	12.	140.	25.
Pb	130.	52.	40.	54.	42.
Hg	0.43				



TABLE 9

## DISTRIBUTION OF TRACE METALS IN THE ENVIRONMENT

ug/g

<u>Metal</u>	<u>Lithosphere<sup>a</sup></u>	<u>Illite 35<sup>b</sup></u>	<u>Atlantic Near-Shore<sup>c</sup></u>	<u>Atlantic Deep-Sea<sup>d</sup></u>	<u>Pacific Deep-Sea<sup>e</sup></u>	<u>-230 Mesh Bulk Sample from Massachusetts Bay</u>
Cr	200	113	100	80	93	310
Cu	70	60	48	115	740	58
Pb	16	53	20	52	150	130
Ni	100	80	55	79	320	63
Mn	1000	275	850	3982	12,500	550
Co	40	45	13	39	160	57
Zn	80	86	95	--	170*	100
Cd	0.18	--	--	--	--	11
Hg	0.5	0.158+	0.09-1.06+	--	--	0.43

-- Not determined

a (87)      d (89)      + (82)

b (80)      e (90)      \* (91)

c (88)

at normal concentrations.

The -230 mesh material was investigated by X-ray diffraction and found to contain  $\alpha$ -quartz as the predominant mineral. Considering that a large majority of the material is silt, rather than clay sized, this finding was expected. Positive identification of illite was possible, and tentative identification of chlorite was made. Interpretation was complicated by the numerous strong lines of  $\alpha$ -quartz, but it was not deemed of sufficient importance to separate the clay from the silt in order to pursue the identification of clay minerals.

In order to obtain an estimate of the maximum possible concentrations of major and minor elements which could be released to the water column, both 0.1 M and 0.5 M HCl extractions were performed on the bulk sediment in triplicate. This information is also useful in speculations about the source of various elements. Difficultly soluble natural minerals will not release large fractions of most elements when leached with dilute HCl. However, deposits from man's activities are likely to be present on the surfaces of minerals or in organic remains. Of course some naturally occurring minerals, especially carbonates and sulfides, are soluble in dilute HCl. Still, the percent of the total amount of an element which is soluble in dilute HCl offers some indication of possible pollution. The data are summarized in Table 8, along with percentages of the total concentration found to be soluble in each of the two acids. For all extractions there was an excess of HCl present. The average relative standard deviation (RSD) for the total analyses was 3.0% for the major elements and 4.1% for the minor elements. For the 0.1 M HCl extractions, RSD was 15% for both the major and the minor elements. For the 0.5 M HCl extractions, RSD was 13% and 9.2% for the major and

minor elements respectively.

Examination of the data in Table 8 provides an order of the elements in terms of the percentage of the total concentration of an element which is soluble in a given acid. For the major elements, the order in 0.1 M HCl was  $\text{Ca} > \text{Fe} > \text{Na} = \text{Mg} = \text{K}$ , while in 0.5 M HCl, the order was  $\text{Ca} > \text{Fe} > \text{K} = \text{Mg} > \text{Na}$ . Calcium was completely soluble in 0.5 M HCl and nearly so in 0.1 M HCl, strongly suggesting its presence as  $\text{CaCO}_3$  and on ion exchange sites. The relatively large amount of soluble iron suggests the presence of hydrous iron oxide which is an excellent adsorbent for most trace metals.<sup>72,73</sup> The amounts of soluble Mg, K and Na were comparatively small indicating that the bulk of these elements was within the lattice of insoluble minerals.

For the trace metals, the orders were nearly the same in both 0.1 M HCl and 0.5 M HCl. The major change was the relative position of lead in the series because it showed approximately the same percent solubility in both acids while the solubility of chromium, copper, and zinc all increased substantially in the 0.5 M HCl relative to the 0.1 M HCl. The only other element which showed minimal increase in solubility in the more concentrated acid was cadmium. The actual orders were  $\text{Zn} > \text{Pb} = \text{Cu} > \text{Cr} > \text{Ni} = \text{Mn} > \text{Cd} > \text{Co}$  for 0.1 M HCl and  $\text{Zn} = \text{Cu} > \text{Cr} = \text{Pb} > \text{Mn} > \text{Ni} > \text{Cd} = \text{Co}$  for 0.5 M HCl. While it is not anticipated that these amounts of metals would actually be released to the water column under normal environmental circumstances, it does indicate that several of the metals are readily rendered soluble by rather mild acid treatment. For zinc, the most common mineral is  $\text{ZnS}$ , but this mineral could not be present because the concentration of sulfide was determined to be less than 2 ug/g. Other soluble zinc minerals could be present but there seems to be strong evidence for possible contamination from man's activities. Rather similar arguments

apply to copper. In contrast, cadmium presents a real paradox. The total concentration is well above the abundance in the lithosphere but only about 10% is soluble in HCl, suggesting that it is present as stable minerals rather than contamination by pollution.

The CEC of the bulk sample was estimated by calcium saturation to be 9.0 meq/100 g. This value was expected to be low due to the abundance of  $\alpha$ -quartz which has a very small CEC, and from the small amount of organic carbon (1.61%) present. The quartz could have been largely removed from the -230 mesh material but this was not done according to the guidelines of NOMES project. Consequently, a large amount of bulk sediment was required in the equilibrium study to make certain that the exchange and/or adsorption capacity of the sediment was in excess relative to the added trace metals.

The ECS was determined by ammonium acetate leaching. Calcium was the most abundant exchangeable cation, followed by magnesium, potassium and sodium. This agrees with the expected order because Ca and Mg being divalent tend to occupy most of the exchange sites. Further, some of the calcium may have been contributed by dissolution of  $\text{CaCO}_3$  in ammonium acetate. The ECS value was calculated to be 11 meq/100 g which is in close agreement with the CEC. In theory CEC should be greater than ECS, but it must be remembered that CEC is dependent on the saturating cation employed. This accounts for the difference observed.

The amount of organic matter which has a very important effect on trace metal adsorption due to its large CEC was determined from both wet oxidation and combustion techniques. The values obtained agreed very well resulting in an average of 1.61%. The nitrogen content was 0.49%. Organic carbon has recently been correlated with organic nitrogen to produce a

new empirical "statistic" called the organic sediment index, OSI.<sup>83</sup>

The OSI= (organic carbon) (organic nitrogen). . .(6)  
and is used in classification of marine sediments.

For the bulk sample,

$$\text{OSI} = (1.61) (0.49) = 0.79 \dots (7)$$

This value predicts that the organic matter is composed of organic detritus, peat, and partially stabilized sludge. Since it is very difficult to isolate and identify the components of sediment organic matter, this index is a useful measure of degree of decomposition.

Assurance that the bulk sample was similar to the core samples from the dredge site was based on the similarity of analytical results. For example, the % organic carbon for the core samples ranged from 0.55 to 2.07%. In similar fashion, the range of values of 0.1 M HCl soluble metals for the cores included the values for the bulk sample in every case except chromium, where the bulk sample was slightly higher than the highest core sample. X-ray analyses showed the same minerals to be present except that some core samples contained significant amounts of aragonite, a very soluble form of  $\text{CaCO}_3$ .

### Equilibrium Experiments

Before attempting any investigation of the adsorptive properties of the bulk sediment, an experiment was conducted to determine if the trace metals were desorbed while being agitated in sea water. This experiment was conducted at both 20°C and at 4°C using a concentration of 15 grams of -230 mesh sediment per liter of sea water. Agitation was accomplished with magnetic stirring. After three hours, the sea water was

separated from the sediment by filtration, and the concentrations of Cu, Pb, Ni, Co, Cd, and Zn were determined in each filtrate and a portion of the same sea water used for the experiment. Results are summarized in Table 10. Each datum represents the average of independent duplicate determinations. It is apparent that none of the trace metals were desorbed during a three-hour equilibration, confirming that sediment preparation procedures had not disturbed the established equilibrium.

In preparation for a study of the effects of environmental factors on adsorption of trace metals from spiked sea water, preliminary experiments were conducted at room temperature with no attempt to control the oxygen level of the sea water. These experiments were conducted in a four-gallon polypropylene bucket containing 10 liters of suspension at a concentration of 15 g/l of -230 mesh sediment. Agitation was accomplished with a motor-driven polypropylene stirrer. At the start of the experiment, the suspension was spiked with 100 ug/l of each of the six elements. Samples were withdrawn after 30 minutes and then every hour on the hour for seven hours. The results, in terms of percent adsorption of added metal as a function of time, based on triplicate trials, are plotted for cobalt, nickel, and cadmium in Figure 7 and for zinc, copper, and lead in Figure 8. Very strong adsorption was observed for copper, lead, and cadmium; moderately strong adsorption was observed for zinc, and significantly weaker adsorption for cobalt and nickel.

It is likely that the adsorption process was incomplete for the less strongly adsorbed metals. Therefore, duplicate six-day equilibrations were conducted in four liter polypropylene beakers. In Table 11, a comparison is made between the residual concentration of the various metals in solution after seven hours and after six days with the

TABLE 10

## DESORPTION OF METALS FROM BULK SEDIMENT AFTER THREE HOURS

<u>Metal</u>	<u>ug/l</u>		
	<u>20°C</u>	<u>4°C</u>	<u>Sea Water</u>
Cu	1.5	1.5	1.5
Pb	2.0	2.0	2.0
Ni	2.0	1.6	2.0
Co	1.0	1.0	1.0
Cd	1.0	1.0	1.0
Zn	1.8	2.2	2.4

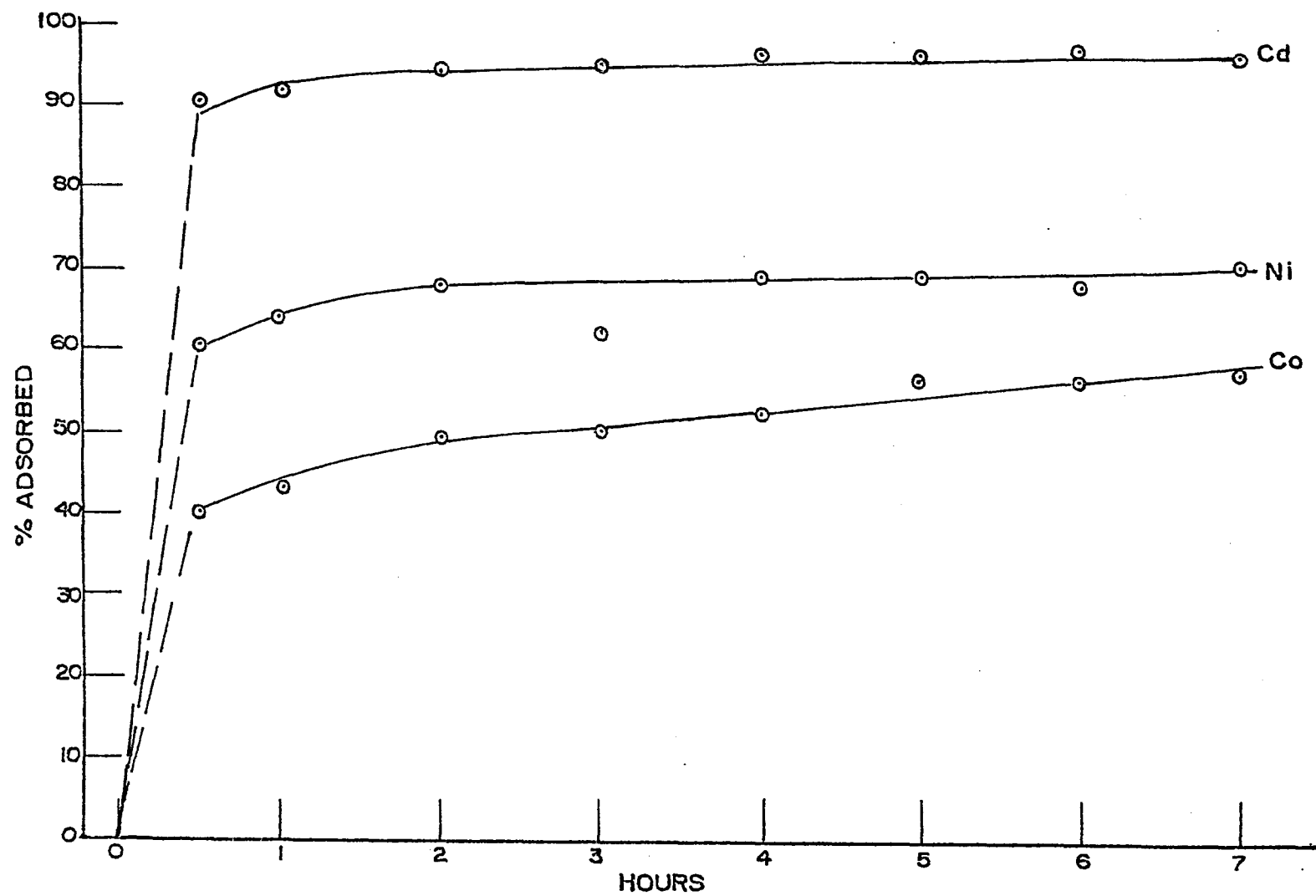


Fig. 7 Per Cent Adsorbed of Added Metal as a Function of Time for Co, Ni, and Cd



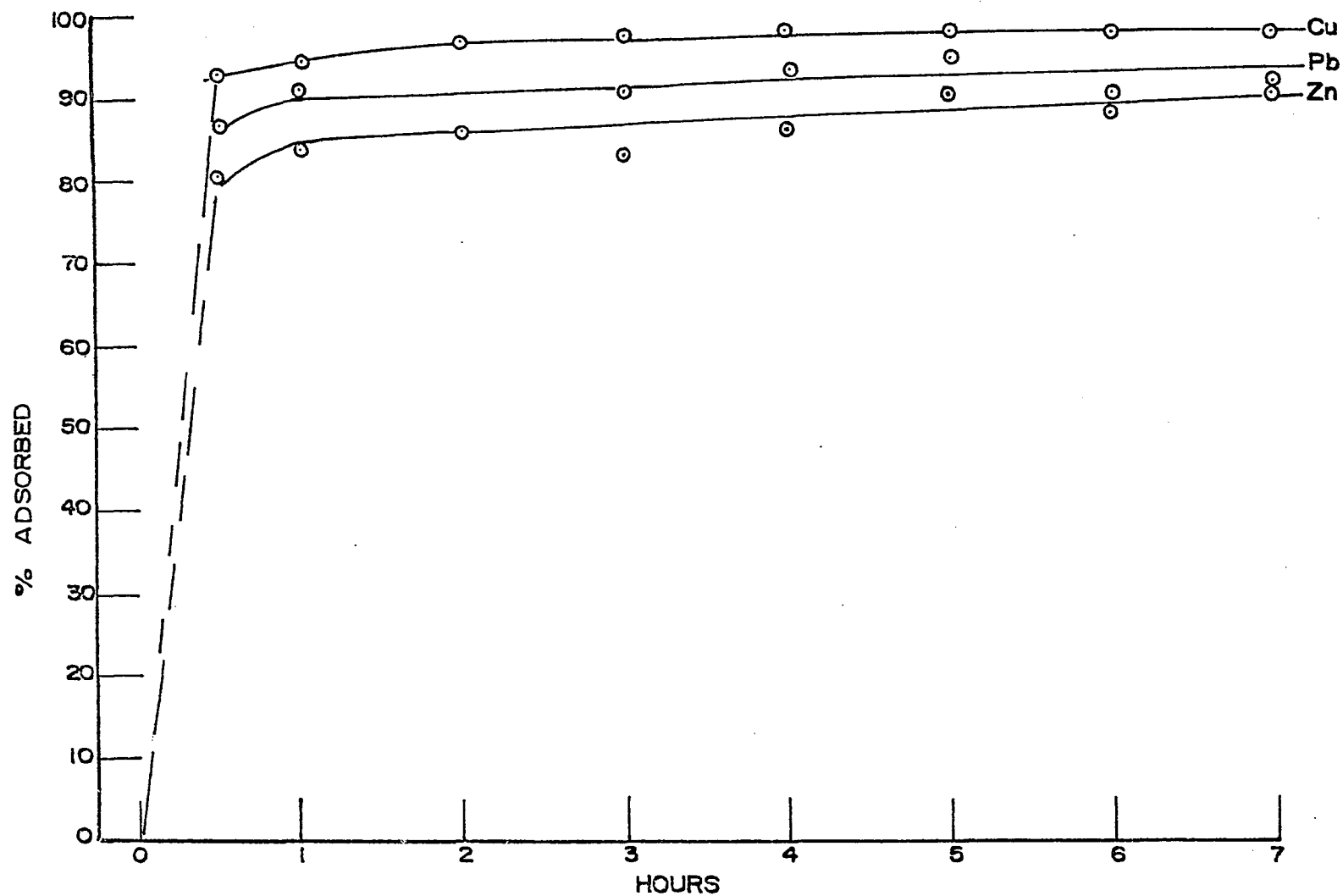


Fig. 8 Per Cent Adsorbed of Added Metal as a Function of Time for Zn, Pb, and Cu

TABLE 11

COMPARISONS OF METAL CONCENTRATIONS  
AFTER SEVEN HOURS AND SIX DAYS EQUILIBRATION  
AT 25°C WITH SEA WATER

<u>Metal</u>	<u>ug/l in Solution after Spiking with 100 ug/l</u>		<u>Normal Sea Water Concentration ug/l</u>
	<u>Seven Hours</u>	<u>Six Days</u>	
Cu	2.0	2.5	1.9
Pb	6.5	2.8	2.4
Ni	30.	11.	1.8
Co	43.	10.	1.0
Cd	3.0	3.0	1.0
Zn	10.	4.2	2.1

experimentally determined concentrations in the sea water used for these experiments. For copper and cadmium, no significant change in concentration was observed between seven hours and six days. For lead and zinc, there was a small but significant decrease in concentration, while nickel and cobalt exhibited a large decrease in concentration between seven hours and six days. The six-day equilibrium concentrations for copper and lead are not significantly different from the concentrations in normal sea water. In the case of cadmium and zinc, the six-day equilibrium samples showed small increases over normal sea water. In contrast, nickel and cobalt showed substantially larger concentrations than normal sea water, strongly suggesting that equilibrium for these two elements was not reached in six days.

A  $2^3$  factorial experiment was designed to investigate the effects of temperature, oxygen concentration, and light level on the rate and amount of adsorption of each of the six metals. Although it was known from preliminary studies that several days were required to reach equilibrium for Co and Ni, it was experimentally impractical to control the several combinations of variables for this length of time. Furthermore, it was important to obtain data for short adsorption times, since preliminary experiments had demonstrated that most of the adsorption occurred during the first hour especially for copper, lead, and cadmium. Each of the eight combinations of high and low settings of the three variables were employed in a three-hour equilibration study using 10 liters of suspension containing 15 g/l of -230 mesh sediment. All batches were spiked with the six metals at a concentration of 100 ug/l. Ten samples were removed for analysis during the three-hour period. In addition, a run was conducted at the high setting of each of the three variables with everything present except

sediment. Analyses showed that no adsorption on the apparatus or other losses of the six metals occurred during the three-hour period.

The method employed to adjust oxygen concentration involved saturating the sea water with air for two hours before a trial was initiated and throughout the three-hour equilibration experiment. For the low level of oxygen, the same procedure was followed except that nitrogen was substituted for air. After the experiments had been completed, it was discovered that the pH of the air-saturated system was much lower than the nitrogen-saturated system. This was due to the greater removal of  $\text{CO}_2$  during nitrogen purging, since the air contained natural levels of  $\text{CO}_2$ . It thus became apparent that the variable originally intended to be oxygen concentration was actually confounded with a change in pH. Consequently, it was necessary to perform a second experiment involving oxygen level and pH before the  $2^3$  factorial experiment could be interpreted.

For the trials involving air saturation, the pH at time zero was 7.60, but it quickly increased to 7.90 where it remained during the balance of three-hour trial. For the runs in which nitrogen saturation was employed, the pH at the outset was 8.06, but it rapidly rose to 8.60 which persisted during the balance of the three-hour equilibration. A  $2^2$  factorial experiment was performed in which the same procedure of air or nitrogen saturation was followed to achieve the high and low levels of oxygen, while pH was adjusted using hydrochloric acid or sodium hydroxide to either 7.90 or 8.60 and maintained at that level throughout the three-hour trial. Independent duplicate runs were made for each of the four combinations of high and low oxygen and high and low pH. Samples were withdrawn after three hours, filtered and the

filtrate analyzed for nickel, cobalt, cadmium and zinc. Lead and copper were not determined because earlier experience had shown that they were so strongly adsorbed that it was very difficult to obtain statistically significant data. Zinc values had to be discarded due to an unknown source of variable contamination. However, the similar response to oxygen concentration in the  $2^3$  factorial for zinc, cadmium, cobalt, and nickel minimized the importance of acquiring data on all of the elements.

The design matrix for this experiment is presented in Table 12 along with the results for nickel, cobalt, and cadmium. Analysis of variance (Table 13) indicated that increasing oxygen concentration from 1.5 to 7.0 mg/l produced a small positive effect on all three elements. None of the increases were statistically significant at the 95% probability level. In contrast, as the pH decreased from 8.6 to 7.9, the concentrations of all three elements remaining in solution increased substantially as shown by the extremely large F ratios. These values are all significant at the 99% probability level. Stated another way, the extent of adsorption increased at the higher pH. No evidence of interaction between oxygen concentration and pH was found. In view of these results, it was concluded that the oxygen variable in the  $2^3$  factorial experiments was really a pH variable; it will be so designated in further discussions.

The  $2^3$  factorial design matrix and the residual concentrations of the six trace metals in solution as a function of time appear in Tables 14 through 19. In Figure 9, the results for cadmium are plotted in terms of percent of the spiked addition which was adsorbed versus time for four combinations of the independent variables. At 20°C, rapid systematic increases in adsorption occurred during the first 30

TABLE 12

EFFECTS OF OXYGEN CONCENTRATION AND pH ON THE ADSORPTION OF SPIKED Co, Ni, AND Cd  
FROM SEA WATER AT 20°C

$2^2$ Design Matrix			Concentrations of Elements Remaining in Solution after Three Hours, ug/l*		
<u>Trial</u>	<u>Oxygen**</u>	<u>pH***</u>	<u>Co</u>	<u>Ni</u>	<u>Cd</u>
1	-1	-1	18, 16	16, 14	3.5, 3.0
2	+1	-1	21, 18	14, 17	3.5, 3.0
3	-1	+1	38, 35	26, 29	5.0, 5.2
4	+1	+1	42, 40	28, 31	6.0, 6.2

\* Duplicate measurements obtained from completely independent trials.

\*\* For oxygen, -1 = 1.5 mg/l and +1 = 7.0 mg/l.

\*\*\* For pH, -1 = 8.6 and +1 = 7.9.

TABLE 13

## ANOVA FOR THE OXYGEN AND pH EXPERIMENT

	<u>Cobalt</u>		<u>Nickel</u>		<u>Cadmium</u>	
	<u>Effect</u>	<u>F</u>	<u>Effect</u>	<u>F</u>	<u>Effect</u>	<u>F</u>
Oxygen Concentration	+3.5	7.53	+1.3	0.81	+0.50	6.84
pH	+20.5	258.**	+13.3	91.**	+2.4	151.**
Oxygen Concentration - pH Interaction	+1.0	0.60	+0.75	0.29	+0.5	6.84
F. <sub>.95</sub> (1,4) = 7.71      F. <sub>.99</sub> (,4) = 21.2						

\*\* These effects are statistically significant at the 99% probability level. No other effects are significant, even at the 95% probability level.

Table 14

Cadmium Concentrations in the  $2^3$  Factorial Experiment

Temperature	-1	+1	-1	+1	-1	+1	-1	+1
pH	-1	-1	+1	+1	-1	-1	+1	+1
Light	-1	-1	-1	-1	+1	+1	+1	+1

## Concentration Remaining in Solution, ug/l

Time  
(minutes)

START	100	100	100	100	100	100	100	100
3	42	40	36	39	17	20	44	19
7	42	28	49	33	18	31	49	22
13	38	19	39	28	19	23	53	26
20	46	13	52	21	20	14	48	37
30	45	9.0	48	16	29	11	47	35
50	60	5.0	47	12	31	7.2	47	22
70	50	3.0	42	9.3	35	5.1	57	18
90	47	2.5	52	7.2	39	5.0	53	15
120	49	1.5	47	4.0	32	4.0	70	9.0
180	36	1.0	42	2.0	24	2.5	70	6.0

Temperature: -1 = 4°C; +1 = 20°C

pH : -1 = 8.6; +1 = 7.9

Light : -1 = Dark; +1 = Light (~ 4000 Lux)



Table 15

Nickel Concentrations in the  $2^3$  Factorial Experiment

Temperature	-1	+1	-1	+1	-1	+1	-1	+1
pH	-1	-1	+1	+1	-1	-1	+1	+1
Light	-1	-1	-1	-1	+1	+1	+1	+1

## Concentration Remaining in Solution, ug/l

Time  
(minutes)

START	100	100	100	100	100	100	100	100
3	83	59	63	51	76	61	87	66
7	80	54	65	45	74	56	81	60
13	74	50	65	44	69	53	82	55
20	78	50	65	45	66	46	86	55
30	75	46	65	40	63	45	84	51
50	73	42	66	40	57	41	81	47
70	75	41	64	39	62	37	81	45
90	71	39	68	38	68	32	79	43
120	68	35	63	34	62	28	81	41
180	64	30	61	33	58	26	77	37

Temperature: -1 = 4°C; +1 = 20°C  
 pH : -1 = 8.6; +1 = 7.9  
 Light : -1 = Dark; +1 = Light (~ 4000 Lux)

Table 16

Zinc Concentrations in the  $2^3$  Factorial Experiment

Temperature	-1	+1	-1	+1	-1	+1	-1	+1
pH	-1	-1	+1	+1	-1	-1	+1	+1
Light	-1	-1	-1	-1	+1	+1	+1	+1

## Concentration Remaining in Solution, ug/l

Time  
(minutes)

START	100	100	100	100	100	100	100	100
3	71	19	66	19	54	17	78	32
7	68	20	67	17	51	17	77	28
13	67	17	64	15	50	15	80	28
20	77	15	64	14	46	14	83	27
30	77	11	65	16	44	11	83	27
50	77	11	69	16	32	10	79	21
70	77	9.7	66	9.0	56	9.0	73	20
90	65	11	73	11	62	5.2	73	20
120	57	7.1	67	8.2	54	6.9	78	15
180	54	5.8	64	7.0	54	6.0	72	13

Temperature: -1 = 4°C; +1 = 20°C

pH : -1 = 8.6; +1 = 7.9

Light : -1 = Dark; +1 = Light (~ 4000 Lux)

Table 17

Cobalt Concentrations in the 2<sup>3</sup> Factorial Experiment

Temperature	-1	+1	-1	+1	-1	+1	-1	+1
pH	-1	-1	+1	+1	-1	-1	+1	+1
Light	-1	-1	-1	-1	+1	+1	+1	+1

## Concentration Remaining in Solution, ug/l

Time  
(minutes)

START	100	100	100	100	100	100	100	100
3	85	76	78	73	80	80	96	84
7	84	73	79	68	78	77	92	82
13	81	70	75	70	76	76	94	78
20	82	70	78	68	78	75	95	78
30	80	65	74	63	76	73	92	78
50	82	64	77	63	72	67	91	73
70	82	62	75	62	74	63	92	72
90	82	61	78	60	78	60	89	70
120	79	57	72	55	76	56	92	66
180	76	51	71	53	74	50	91	62

Temperature: -1 = 4°C; +1 = 20°C

pH : -1 = 8.6; +1 = 7.9

Light : -1 = Dark; +1 = Light (~ 4000 Lux)

Table 18

Lead Concentrations in the  $2^3$  Factorial Experiment

Temperature	-1	+1	-1	+1	-1	+1	-1	+1
pH	-1	-1	+1	+1	-1	-1	+1	+1
Light	-1	-1	-1	-1	+1	+1	+1	+1

## Concentration Remaining in Solution, ug/l

Time  
(minutes)

START	100	100	100	100	100	100	100	100
3	5.0	3.8	4.2	5.9	9.0	8.7	13	5.9
7	5.0	4.4	4.2	6.7	7.0	7.0	13	7.7
13	3.8	5.0	4.8	5.9	6.3	5.3	13	5.3
20	6.2	3.2	4.2	5.9	5.7	4.5	13	5.9
30	6.2	3.2	6.0	2.6	6.3	6.2	13	5.9
50	6.2	3.8	5.4	2.6	6.3	5.3	10	5.3
70	6.2	3.2	5.4	2.6	4.3	7.0	11	5.3
90	3.8	5.0	4.8	2.6	5.0	3.6	10	5.3
120	6.2	3.8	4.2	1.8	5.7	3.6	10	4.1
180	6.2	5.0	4.2	1.0	6.3	2.8	7.0	5.3

Temperature: -1 = 4°C; +1 = 20°C

pH : -1 = 8.6; +1 = 7.9

Light : -1 = Dark; +1 = Light ( ~ 4000 Lux)

Table 19

Copper Concentrations in the  $2^3$  Factorial Experiment

Temperature	-1	+1	-1	+1	-1	+1	-1	+1
pH	-1	-1	+1	+1	-1	-1	+1	+1
Light	-1	-1	-1	-1	+1	+1	+1	+1

## Concentration Remaining in Solution, ug/l

Time  
(minutes)

START	100	100	100	100	100	100	100	100
3	2.4	2.5	1.9	2.6	3.1	3.3	2.5	2.4
7	1.2	2.1	1.9	2.6	2.9	3.6	2.5	1.9
13	1.2	2.8	1.9	2.6	3.4	3.0	2.2	1.9
20	1.2	3.3	2.3	2.6	2.9	3.0	2.5	1.9
30	1.5	2.8	4.1	7.0	3.6	3.3	2.5	2.9
50	1.7	2.5	8.6	1.6	2.9	3.0	2.8	1.9
70	1.5	2.8	1.9	7.2	2.6	3.3	2.2	2.4
90	1.5	6.7	1.4	2.6	2.4	2.5	2.8	2.4
120	2.4	2.8	1.0	2.1	2.6	3.6	5.0	4.2
180	1.5	2.8	1.9	2.1	2.6	4.1	2.8	3.2

Temperature: -1 = 4°C; +1 = 20°C

pH : -1 = 8.6; +1 = 7.9

Light : -1 = Dark; +1 = Light (~ 4000 Lux)

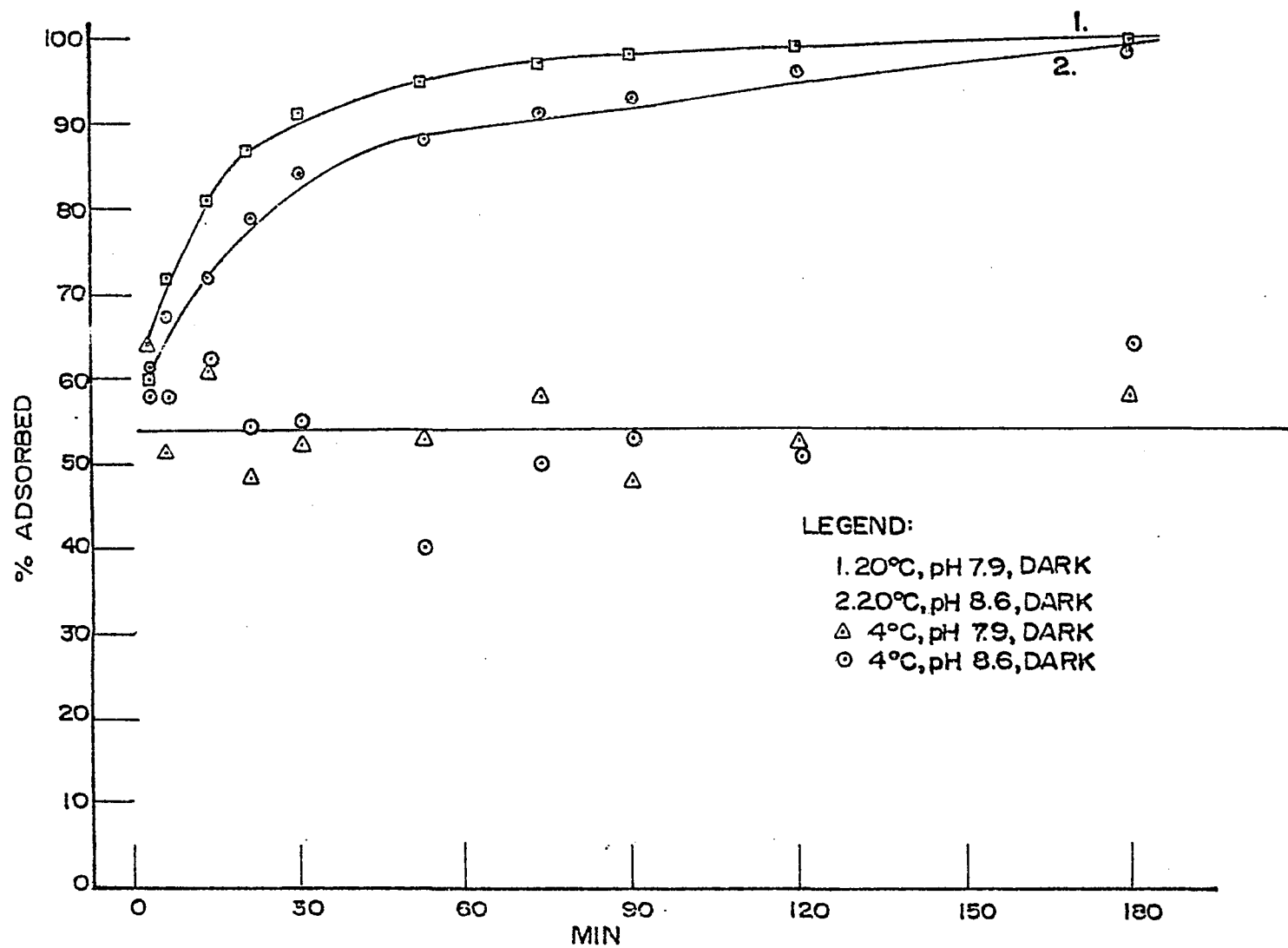


Fig. 9 Per Cent Cadmium Adsorbed versus Time at Four Conditions of the Factorial Experiment

minutes with a gradual approach to nearly complete adsorption after three hours. In contrast, the two trials at 4°C showed a wide scatter with no significant change in percent adsorption after the first three minutes of the equilibration period which represents the earliest time at which a sample could be obtained. A major systematic difference is attributable to the difference between 20°C and 4°C.

Results are depicted for nickel in Figure 10. Here there was much less adsorption than for cadmium at both temperatures, and it appears unlikely that true equilibrium was reached for any of the four conditions. The large difference in behavior at 20°C compared to 4°C is again obvious.

The adsorption data for all the metals were examined to determine if they could be fitted to either first or second order kinetic models. Only the cadmium results at 20°C seemed to fit either of these models. In Figure 11, the second order models for the cadmium trials at 20°C in the dark are plotted. At a pH of 7.9, results for the first 80 minutes of equilibration fit a reasonable linear model with a rate constant of  $1.8 \times 10^5 \text{ liter mole}^{-1} \text{ min.}^{-1}$ . At a pH of 8.6, the linear model only holds through the first 30 minutes of equilibration with a rate constant of  $3.6 \times 10^5 \text{ liter mole}^{-1} \text{ min.}^{-1}$ . The intercepts for both curves are reasonably close to 0.01 which correspond to 100 ug/l at  $t=0$ .

No ANOVA was conducted on the data for lead and copper (Tables 18 and 19) because the concentrations for both of these elements approached the background level of sea water in the first few minutes and showed only random variations throughout the complete three-hour equilibrations. This finding agrees with the observations of Krauskopf<sup>72</sup> working at higher concentrations in sea water systems and with Schnitzer<sup>70</sup> who reported that the highest stability constants for complexes

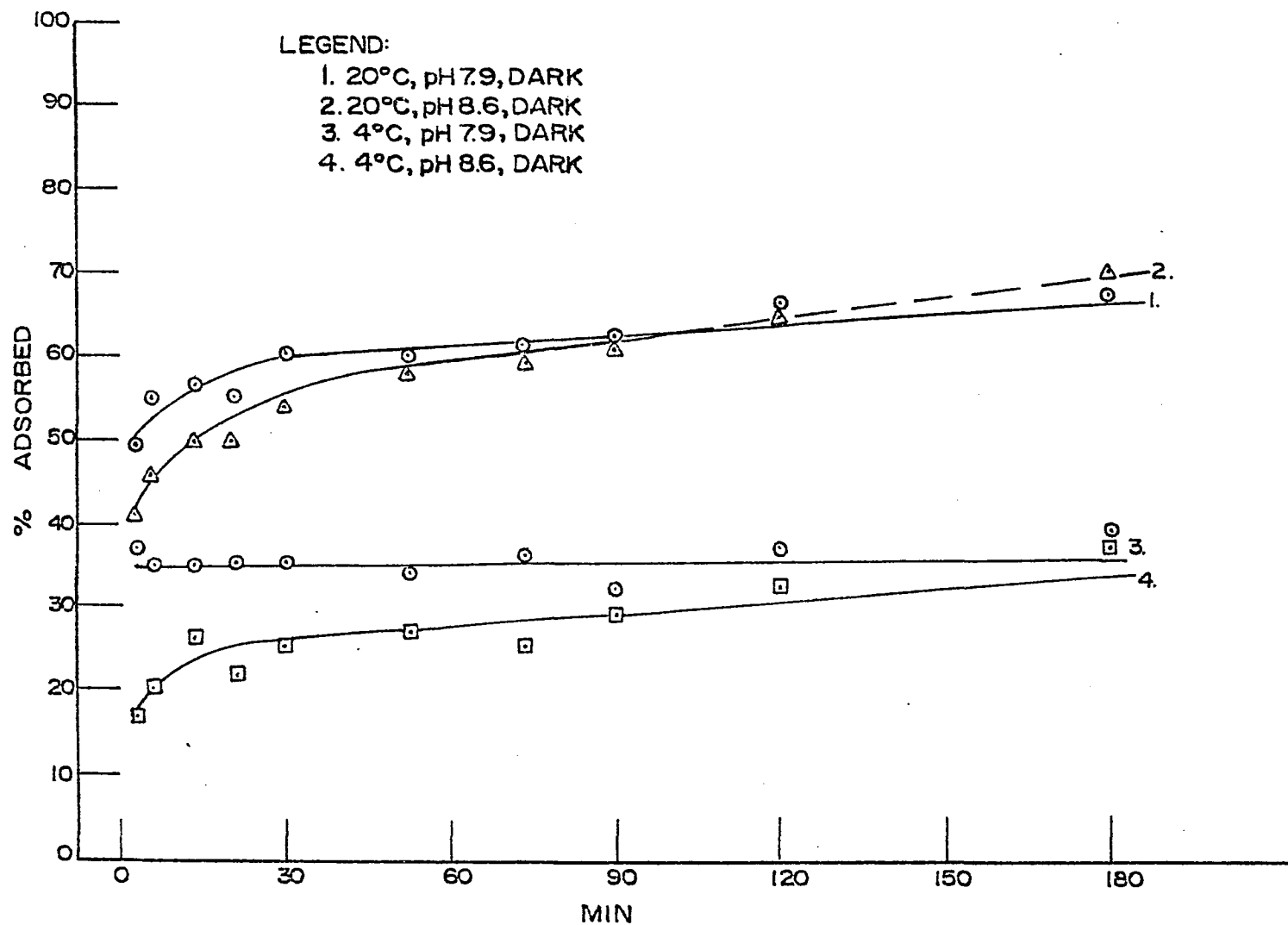


Fig. 10 Per Cent Nickel Adsorbed versus Time at Four Conditions of the Factorial Experiment



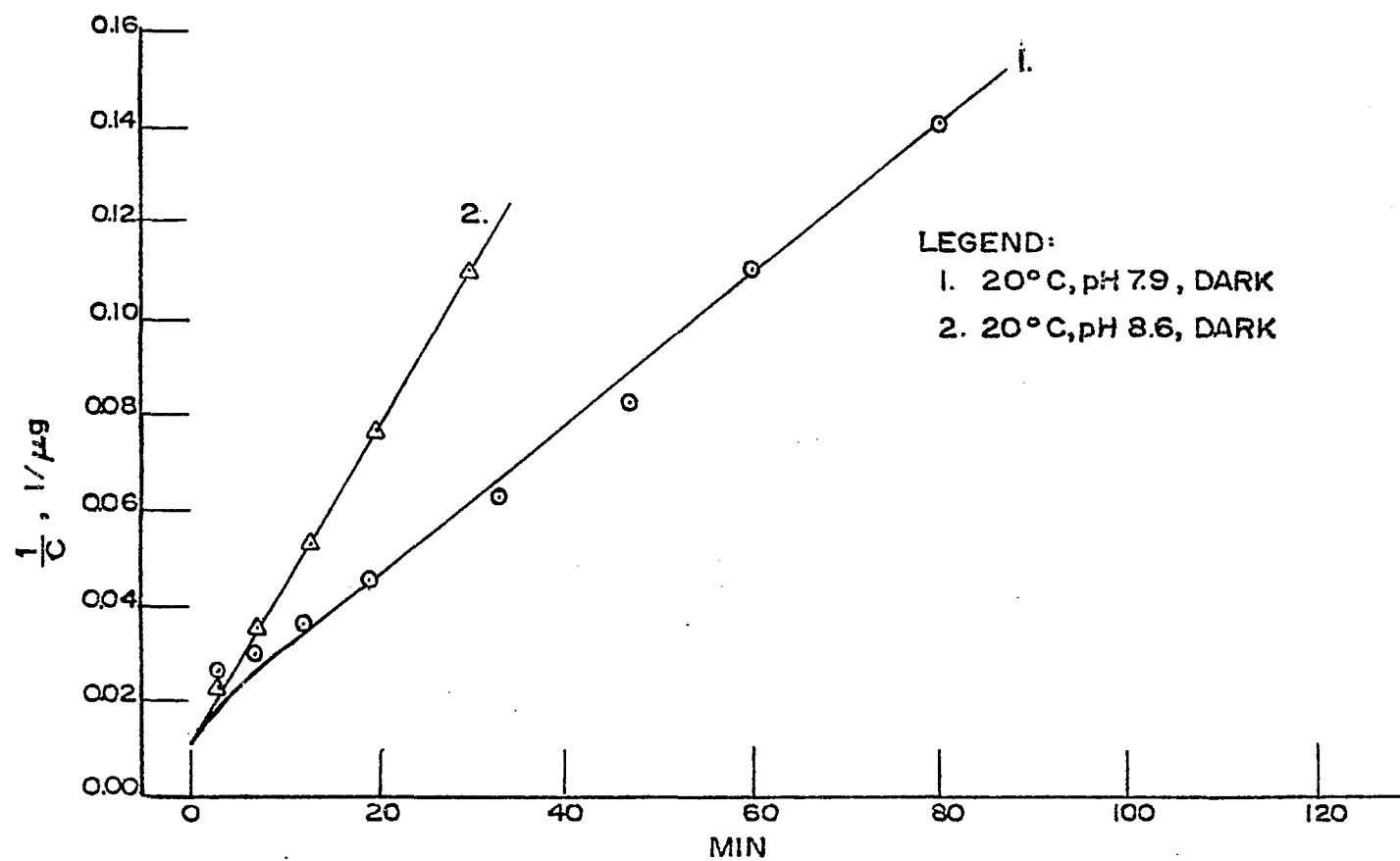


Fig. 11 Second Order Kinetic Plots for Cadmium

in soils were found for copper and then lead.

In order to conduct ANOVA on the other four elements, an estimate of error was required. Since the concentrations showed a close approach to equilibrium at three hours, the possibility of using the two-hour and three-hour measurements as duplicates was investigated. For this purpose, a paired "t" test was run on each of the four elements for the eight different combinations of environmental factors. The calculated "t" values with seven degrees of freedom were 6.63, 4.34, 3.28, and 2.62 for nickel, cobalt, zinc, and cadmium, respectively. The tabular value at the 95% probability level for seven degrees of freedom is 2.37. Thus, we must conclude that there are systematic differences between the two-hour and three-hour values for all four elements, although the differences are quite small, ranging from an average of 4 down to 2 ug/l. Consequently, it was decided to use the two-hour and three-hour values as duplicates with the knowledge that this would produce an error estimate which was biased on the high side, thereby desensitizing the ANOVA. Under these conditions, conclusions about the significance of environmental factors are conservative due to the inflated value for the error mean square.

Also, two replicate trials conducted at 4°C, low pH, light and at 20°C, high pH, dark were in good agreement with the previous trials run under the same conditions. Differences in concentrations remaining in solution after three hours, between these trials and those run earlier, were of the same magnitude as the 2 and 3 hour data used as duplicates in the ANOVA. Considering the total analytical error involving sampling, pipetting, and the analytical determination, it would appear that the use of the 2 and 3 hour data as duplicates still represent a fair estimate of the error.

ANOVA results are summarized in Table 20. The temperature effect was always negative and significant at the 99.9% probability level. This means that much lower concentrations of the four metals remained in solution at 20°C than at 4°C. The reduced amount of adsorption at lower temperature agrees with Chester's findings for cobalt adsorption on illite in sea water<sup>74</sup>, but is contrary to his findings for zinc in the same system. However, it should be kept in mind that, in Chester's experiments, adsorption undoubtedly occurred primarily by an ion exchange mechanism since he was using a pure clay system; whereas these results were obtained on a natural sediment containing organic matter which permits many other mechanisms of adsorption besides ion exchange.

The effect of changing pH from 8.6 to 7.9 is to increase the residual concentration of metal in solution. Stated another way, adsorption is greater at the higher pH setting in all cases. The difference is statistically significant at the 99.9% level for nickel, cadmium, and zinc and at the 99% probability level for cobalt. Kurbatov<sup>67</sup> reported increased adsorption of cobalt on freshly precipitated hydrous ferric oxide as the pH increased, and Schnitzer<sup>70</sup> reported that the stability constants for lead, copper, zinc, cobalt, and nickel with fulvic acid increased markedly as the pH was increased from 3.5 to 5. No measurements were reported at higher pH values, but the increased ionization of organic compounds such as humic and fulvic acids would tend to promote metal complex formation. Unfortunately, other experimental data for comparison could not be found.

The adsorption behavior is also consistent with the findings reported earlier in this work in which the percentage of free ionic copper was found to decrease markedly as pH was

TABLE 20  
ANOVA FOR 2<sup>3</sup> FACTORIAL EXPERIMENT

	<u>Cobalt</u>		<u>Nickel</u>		<u>Cadmium</u>		<u>Zinc</u>	
	<u>Effect</u>	<u>F</u>	<u>Effect</u>	<u>F</u>	<u>Effect</u>	<u>F</u>	<u>Effect</u>	<u>F</u>
Temperature	-23.	306.***	-34.	744.***	-43.	423.***	-54.	3009.***
pH	+5.4	17.**	+7.0	32.***	+13.	37.***	+9.8	101.***
Light	+6.6	25.***	+2.8	4.9	+4.4	4.5	+3.6	14.**
Temp-pH	+.13	0.01	-0.50	0.2	-9.5	21.**	-5.6	33.***
Temp-Light	-2.1	2.7	-2.8	4.9	-1.1	0.3	-0.4	0.1
pH-Light	+8.4	42.***	+8.5	47.***	+11.	26.***	+4.4	20.**
Temp-pH-Light	-2.9	4.94	-3.0	5.9*	-9.4	21.**	-1.1	1.3
F <sub>.95</sub> (1,8) = 5.32			F <sub>.99</sub> (1,8) = 11.26			F <sub>.999</sub> (1,8) = 25.42		

\* Significant at 95% probability level

\*\* Significant at 99% probability level

\*\*\* Significant at 99.9% probability level

elevated from 7 to 9. If we accept the model of Zirino and Yamamoto<sup>23</sup>, the principal species formed as pH increases is  $\text{Cu}(\text{OH})_2^0$  which could precipitate within the matrix of both inorganic and organic portions of the sediment. Similar considerations apply to the other metals.

The effect of light levels was consistent to the extent that the average adsorption was always numerically greater in the dark than in the light. However, this effect was only significant for cobalt (99.9% probability level) and zinc (99% probability level). The F ratios for both nickel and cadmium were just slightly below the required tabular values at the 95% probability level. No explanation for this phenomenon can be offered. The significant interaction between pH and temperature for zinc and cadmium is caused by the greater effect of pH at 4°C than at 20°C. There is no reversal of direction, only a change in magnitude. The significant interaction of pH and light for Co, Ni, Zn, and Cd is due to the large pH effect in light compared with the effect of pH in the dark. At present, no physical or chemical rationale for these interactions can be suggested.

In all equilibrium experiments the order of trace metal adsorption was the same. The order (Table 21) was  $\text{Cu} = \text{Pb} > \text{Cd} > \text{Zn} > \text{Ni} > \text{Co}$  which is in general agreement with Krauskopf's<sup>72</sup> adsorption studies in sea water using several different adsorbents. He stated that the concentrations of Cu, Pb, and Zn were reduced within a few hours nearly to the range found in sea water. These findings are in accord with the results obtained in this work for Pb and Cu at 4°C and 20°C and for Zn and Cd at 20°C. Adsorption studies of Cd were planned by Krauskopf but were omitted due to analytical difficulties in determining the small concentrations remaining after adsorption. He suggested, however, that Cd might behave

TABLE 21

## ORDER OF ADSORPTION AFTER THREE HOURS

<u>Experimental Conditions</u>	<u>Order Adsorbed (% adsorbed)</u>
20°C, pH 7.9, Dark	Cu=Pb=Cd > Zn > Ni > Co 98=99=98 > 93 > 67 > 47
4°C, pH 7.9, Dark	Cu=Pb > Cd > Zn=Ni > Co 98=96 > 58 > 36=39 > 29
20°C, pH 8.6, Dark	Cu=Pb=Cd > Zn > Ni > Co 97=95=99 > 94 > 70 > 49
4°C, pH 8.6, Dark	Cu=Pb > Cd > Zn > Ni > Co 98#94 > 64 > 46 > 36 > 24
4°C, pH 7.9, Light	Cu=Pb > Cd=Zn > Ni > Co 97=93 > 30=28 > 23 > 9
20°C, pH 8.6, Light	Cu=Pb=Cd=Zn > Ni > Co 96=97=97=94 > 74 > 50
4°C, pH 8.6, Light	Cu=Pb > Cd > Zn=Ni > Co 97=94 > 76 > 46=42 > 26
20°C, pH 7.9, Light	Cu=Pb=Cd > Zn > Ni > Co 97=95=94 > 87 > 63 > 38

like Cu, Pb, and Zn because it is a good polarizing ion as are the former ions, possibly because of complete 18-electron shells ( $\text{Cu}^{2+}$  has only 17 electrons). Riemer and Toth<sup>92</sup> found complete adsorption of copper at concentrations up to 2.5 mg/l on kaolinite, illite, montmorillonite, and humic acid, even at low pH.

According to Krauskopf, Co and Ni concentrations found in sea water are most probably controlled by biological mechanisms operating over a long period of time. Such effects would not be noticed in this investigation. Manganese nodules are very good adsorbents for Co and Ni.<sup>22</sup> However, hydrous manganese oxide is unlikely to play a significant role here because of the very small amount of manganese found in this sediment. This may account for the slow adsorption of these elements in this study.

For purposes of the field dredge study, these investigations have shown that the dredge spoils are unlikely to induce significant trace metal contamination to the surface water by a desorption mechanism. Consequently, the major source of trace metal additions to the water will be the dredge apparatus and associated activities. It has been predicted that it may take several days for the very fine sediment to reach the ocean floor in Massachusetts Bay, due to turbulence and strong currents. Considering the rapid adsorption of Pb, Cu, Cd, and Zn on natural sediment for most environmental conditions, it is unlikely that the concentrations of soluble species of these metals will be greatly altered in the water column. It is possible that Ni and Co concentrations could be increased if significant amounts of these metals are added to the water by corrosion or other means. Even here the sediment can be expected to adsorb substantial amounts of these elements, especially during summer when the water is warm. Unless very

large amounts of these metals were released, there should be no detrimental effect on biological organisms.

The findings have further implications concerning other sources of metal pollution in sea water. It is clear that sediment can be very effective in scavenging metals from the water. However, many marine organisms which live in sediment have shown a great capacity to concentrate heavy metals, so the adsorption of metals on sediments does not completely obviate the problem of toxicity to the marine environment. Furthermore, any chemical spill or the development of anoxic conditions could easily produce a rapid release of those metals to the water column.



## SUMMARY

The copper specific ion electrode has been shown to be useful in determining both total (2.2 ug/l) and ionic (0.001 ug/l) concentrations in sea water. Total copper concentration in sea water was measured by known addition methods (known increment scale and Gran's Plots) which compared favorably with the more time-consuming solvent extraction-atomic absorption method. This latter technique, however, has the advantage of providing analyses for several elements simultaneously.

The determination of ionic copper was arduous because of the very small concentration of  $\text{Cu}^{2+}$  present and the difficulty in preparing calibration solutions. Standard solutions containing 100 to 10,000 ug/l ionic copper were made in 0.70 M  $\text{KNO}_3$  as a non-complexing ionic strength medium. A linear response resulted, but extrapolation of the working curve several orders of magnitude was required in order to determine natural levels of ionic copper. More dilute calibrating solutions in the range of 1-10 ug/l ionic copper could be synthesized but would result in (a) a very slow electrode response, (b) possible copper contamination from  $\text{KNO}_3$ , (c) unstable standard solutions due to adsorption onto container walls, and (d) significant complexation of  $\text{Cu}^{2+}$  by the hydroxide anion. Therefore, the extrapolation technique was used in estimating ionic copper concentrations in sea water.

At this stage of development, the copper electrode could not be used for continuous monitoring in natural sea water due to the very small concentration of  $\text{Cu}^{2+}$ . However, it is one of the few devices which can be used to determine

the concentration (activity) of free ionic copper.

Copper was shown to be complexed with the organic matter normally found in sea water and, after its partial extraction with chloroform at pH2, the ionic copper concentration increased about threefold, but still represented only a small percentage ( $\sim 0.1\%$ ) of the total copper present.

The concentration of ionic copper was studied as a function of pH in the range of 7-9. The amount of  $\text{Cu}^{2+}$  decreased as the pH was raised, due to the predicted formation of  $\text{Cu}(\text{OH})_2^0$  at the higher pH.

In related studies, the adsorption of trace metals onto a natural marine sediment taken from Massachusetts Bay was investigated as part of an ocean mining environmental study. In order to characterize the sediment, the -230 mesh material was examined for total and HCl extractable metals (major and minor), organic matter content, cation exchange capacity (CEC), exchangeable cation status (ECS) and mineralogical characterization. The sediment showed higher than normal total concentration of Cr, Pb, and Cd, possibly due to pollution in the area. Biological scavenging, however, is an alternate possibility, especially for Cr and Cd.

Dilute HCl extractions of metals from the sediment were compared to the total concentrations and indicated that Pb, Zn, Cu, and Cr might be present as pollutants since these metals were so readily soluble in the mild acid treatments. Cd, however, was not very soluble in mild acid, suggesting that this metal was present in the crystal lattice of the minerals present, rather than as a pollutant. Analyses of the major cations indicated that much of the iron is probably present as hydrous iron oxide due to its ease of dissolution and that calcium is present on ion exchange sites and as the carbonate. Sodium, magnesium, and potassium extractions

indicated that these metals were primarily within the lattice of insoluble minerals because of the small percentage of these metals extracted in the dilute acid treatments.

The degree of decomposition of the organic matter of this sediment was estimated by calculation of its organic sediment index (OSI) from the product of organic carbon and nitrogen. The organic matter was composed of organic detritus, peat and partially stabilized sludge, according to this classification. The CEC was determined by calcium saturation to be 9.0 meq/100 g which agreed with the experimentally determined ECS. X-ray diffraction analyses showed that the major mineral component was  $\alpha$ -quartz with small amounts of illite, which would account for the small CEC.

To study the effects of environmental factors on the adsorption of trace metals on this -230 mesh sediment, a  $2^3$  factorial experiment was conducted. The independent variables were temperature, oxygen concentration, and light, each factor being controlled at a high and low setting. At the conclusion of these experiments, it was found that the oxygen variable was inadvertently confounded with pH due to the method of controlling the oxygen concentration. In separate experiments, it was determined that pH was the significant independent variable in the  $2^3$  factorial experiments and not oxygen.

Studies on the rate of adsorption of added metal after three hours showed that copper and lead were rapidly adsorbed in the first ten minutes under all conditions. At 20°C, zinc and cadmium were gradually adsorbed and showed near complete adsorption at the end of three hours. However, at 4°C, the rate of adsorption for these two metals was very slow. Cobalt and nickel exhibited widely varying adsorption, which indicated that these two metals are not preferentially adsorbed by this sediment. On the average, cobalt and nickel were adsorbed 34

and 52%, respectively, at the end of three hours.

Temperature was the most important variable affecting the degree of adsorption with the greatest adsorption at the higher temperatures for all metals. Thus, trace metals released in the water column will be adsorbed to a large extent if dredging is conducted in warm waters. There was always greater adsorption at pH 8.6 than at 7.9, probably due to increased ionization of weak organic acids present in the organic matter and possibly through coprecipitation of hydroxides. This fact becomes important when dredging operations disturb anoxic bottom sediments. The components of this type of sediment, which usually contains high concentrations of sulfides, alkyl thiols, and organic matter, are strong metal binding compounds. They are eventually destroyed in oxygen-rich waters, and subsequently release the bound heavy metals.<sup>93</sup> However, these trace metals would be rapidly adsorbed due to the higher pH of surface sea water. The effect of light on adsorption was significant only for cobalt and zinc with greater adsorption in the dark. Unfortunately, no explanation for this phenomenon could be offered. It is unlikely, however, that light or dark conditions have a significant role in controlling adsorption. The significant interaction of pH-temperature and pH-light indicated that these variables were not completely independent. This made interpretation of the effect of these variables more difficult.

In conclusion it is not expected that trace metals found in the water column during ocean mining operations would pose a great threat to the marine community. Trace metals, whatever their source, would be adsorbed in relatively short periods of time, especially in warm waters. Even if acid spills or the production of anoxic conditions at the

ocean floor released considerable amounts of metals, the sediment would act as an efficient scavenger and reduce the concentrations of these metals to non-toxic levels.

However, this silt and clay sized material of the sediment is subject to ingestion by bottom-feeding fish and other benthic organisms and, thus, may contribute heavy metals to the marine food chain.

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